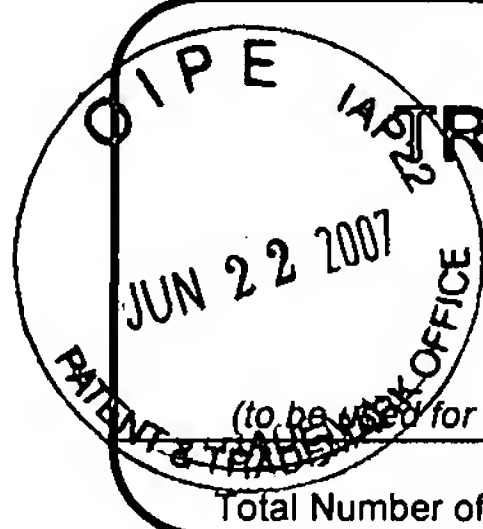


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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Narumi Koga et al

Serial No.: 10/802,652

Filed: March 16, 2004

Art Unit: 2853

Examiner: Shah, Manish S.

Confirmation No.: 3942

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Atty. Docket No.: 501152.20026

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BRIEF ON APPEAL

S I R:

This brief is submitted in support of the Notice of Appeal filed on April 26, 2007, in response to Examiner's Advisory Action Dated April 10, 2007, and the Final Office Action mailed November 27, 2006.

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Serial No: 10/802,652
Atty. Docket No.: 501152.20026

1. REAL PARTY IN INTEREST

The real party in interest in the above-identified application is the Assignee,
BROTHER KOGYO KABUSHIKI KAISHA, 15-1 Naeshiro-cho, Mizuho-ku, Nagoya-shi,
Aichi-ken 467-8561, as evidenced by an Assignment recorded at Reel/Frame No. 015306/0626
for U.S. Application Serial No. 10/802,652.

2. RELATED APPEALS AND INTERFERENCES

No interference is known to the Appellants, the Appellants' legal representative, or Assignee which will directly affect, be directly affected by or have a bearing on the Board's decision in this Appeal.

3. STATUS OF ALL CLAIMS

The above-identified application was filed on March 16, 2004, and claims priority from Japanese Patent Application Nos. 2003-072463, 2003-072464, and 2003-072465, all filed March 17, 2003. The above application was filed with original claims 1-20.

On April 10, 2006, the Examiner issued a Restriction Requirement. Applicants subsequently elected to proceed with claims 13-20.

On May 30, 2006, The Examiner issued an Office Action rejecting claims 13-20 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent Application No. 2003/0195275 to Sanada et al. ("Sanada") in view of U.S. Patent No. 5,116,409 to Moffatt ("Moffatt"). The Examiner also rejected claims 13-18 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent No. 6,485,138 to Kubota et al. ("Kubota") in view of Moffatt. In addition, the Examiner rejected claims 13-20 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent Application No. 2003/0218661 to Okada et al. ("Okada") in view of Moffatt. Applicants filed a response to this Office Action on September 29, 2006. No claims were amended in this response.

Applicants then received a Final Office Action mailed on November 27, 2006. In this Final Office Action, the Examiner modified the Examiner's prior rejections based on new art disclosed by Applicants in an information disclosure statement. In this Office Action, the Examiner rejected claims 13-20 under 35 U.S.C. § 103(a) as being unpatentable over Sanada in view of JP 2001-081372 to Ikemoto et al ("Ikemoto"). The Examiner also rejected claims 13-18 under 35 U.S.C. § 103(a) as being unpatentable over Kubota in view of Ikemoto. In addition, the Examiner rejected claims 13-20 under 35 U.S.C. § 103(a) as being unpatentable over Okada in view of Ikemoto.

On March 14, 2007, in response to this Final Office Action, Applicants submitted a Response containing no claim amendments. Applicants then received an Advisory Action on April 10, 2007. In that Advisory Action, the rejection of claims 13-20 over Sanada in view of

Ikemoto and the rejection of claims 13-18 over Kubota in view of Ikemoto were maintained, while the rejection of claims 13-20 over Okada in view of Ikemoto was withdrawn. A Notice of Appeal was subsequently filed by Applicants on April 26, 2007.

As a result, claims 1-12 stand withdrawn and claims 13-20 are original. Thus, claims 1-20 remain in this application and the rejection of claims 13-20 is hereby appealed.

4. STATUS OF AMENDMENTS

No amendments have been made.

5. SUMMARY OF CLAIMED SUBJECT MATTER

The present invention relates to a water base ink for ink-jet recording to be used for an ink-jet recording apparatus. Application (as filed), ¶ [0001].

In order to perform the satisfactory recording over a long period of time, for example, the following conditions are required for the water base ink for ink-jet recording. Application (as filed), ¶ [0003]. That is, characteristic values including, for example, those of the viscosity, the surface tension, and the density are appropriate values; any deposit is not formed and/or physical values are not changed, for example, by the heat in order to avoid any clog-up at the nozzle and the orifice of the ink-jet recording apparatus so that the ink is discharged in a stable manner; and the recorded image is excellent, for example, in water resistance and light resistance. *Id.*

When the recording is performed with an ink-jet printer by using a general water base ink for ink-jet recording, any exclusive ink-jet paper is sometimes used in order to obtain a satisfactory printing quality without any blurring. Application (as filed), ¶ [0004]. However, in recent years, it is more demanded that the recording is performed on the regular paper rather than on the exclusive ink-jet paper, in consideration of the running cost and the environment. *Id.* Further, in the market directed to homes and offices, it is overwhelmingly demanded that the recording is performed with the colors rather than with the black-and-white or monochrome. *Id.* Therefore, the color ink-jet printer is dominantly used. *Id.* It is demanded that the color recording can be performed with a good printing quality on the regular paper. *Id.*

However, the printing quality on the regular paper is still insufficient. Application (as filed), ¶ [0005]. Major factors therefor may include various factors. *Id.* One of such factors is the problem called “feathering”. *Id.* In this case, the ink is nonuniformly blurred along the paper fibers of the recording paper when the ink is permeated into the recording paper. *Id.* The edges of

image portions are notched, and it is impossible to obtain any sharp edge of the image portion.

Id.

In relation to such circumstances, a method, in which the surface tension is increased to obtain an ink composition that scarcely causes the blurring or spread into the paper fibers of the recording paper, has been hitherto widely known as a general technique for improving the printing quality by avoiding the feathering. Application (as filed), ¶ [0006]. However, in the case of this method, the wettability of the ink with respect to the paper is deteriorated, and ink portions, which are adjacent to one another on the recording paper, are not continued to give a discontinuous state, resulting in such a printing quality that the spread of the ink is insufficient. *Id.* In order to avoid such an inconvenience, it is also conceived that an extremely large amount of the ink is discharged. *Id.* However, in this case, new problems arise, for example, such that the cost is unsatisfactory and the ink is dried over an excessively long period of time. *Id.* Therefore, an ink is required, which is spread appropriately and uniformly with an appropriate amount of droplets. *Id.*

On the other hand, a method has been widely used as a general technique for enhancing the permeability of the water base ink for ink-jet recording, in which mutually adjoining ink droplets are continued to one another on the recording paper to improve the printing quality by blending, as a permeating agent, alkyl ether of polyvalent alcohol such as diethylene glycol monobutyl ether to an ink, or by blending a surfactant thereto. Application (as filed), ¶ [0007]. However, in the case of this method, it is impossible to suppress the phenomenon in which the ink is nonuniformly spread along the paper fibers. *Id.* As a result, the edges of image portions are blurred, and the feathering tends to occur. *Id.*

As described above, the conventional water base ink for ink-jet recording has involved such a problem that it is difficult to satisfy both of the prevention of the feathering and the prevention of the insufficient ink spread on the regular paper. Application (as filed), ¶ [0008].

Further, another problem arises such that the ink is not discharged upon the start of use if the water base ink for ink-jet recording is not introduced smoothly into an ink flow

passage of a printer head when a new ink cartridge is installed to an ink-jet printer. Application (as filed), ¶ [0009]. Therefore, it is also required for the water base ink for ink-jet recording that the initial introduction performance of the ink into the printer head is excellent in addition to the requirements for the prevention of the feathering and the prevention of the insufficient spread of the ink as described above. *Id.*

However, in recent years, the miniaturization is advanced for the printer head for the ink-jet printer. Application (as filed), ¶ [0010]. For example, a stacked or laminated type printer head is known as a printer head for a piezoelectric ink-jet printer based on the use of piezoelectric elements, which is formed by stacking a plurality of sheets formed with parts of ink flow passages. *Id.* In the case of the stacked type printer head, the miniaturization is realized at the low cost, and the ink flow passage, which is narrow and which has a complicated structure, can be formed therein. *Id.* However, bubbles or foams tend to remain at certain portions of the printer head. *Id.* It has been impossible to smoothly introduce the water base ink for ink-jet recording into the ink flow passages, and it has been especially difficult to satisfy the initial introduction performance of the ink. *Id.*

In view of the above, a method is known as a method for improving the initial ink introduction performance of the water base ink for ink-jet recording, in which an appropriate amount of a surfactant is added to the water base ink for ink-jet recording to lower the surface tension down to an optimum value in order to improve the wettability with respect to the inner wall of the ink flow passage of the printer head. Application (as filed), ¶ [0011].

However, in the case of the method in which the surfactant is added to the water base ink for ink-jet recording to lower the surface tension so that the initial introduction performance of the water base ink for ink-jet recording into the ink flow passage is improved, the following problem arises. Application (as filed), ¶ [0012]. That is, the wettability with respect to the recording paper is increased simultaneously with the decrease in the surface tension of the ink, and the edges of image portions are blurred to cause the feathering. *Id.* In other words, the conventional water base ink for ink-jet recording has involved such a problem that it is difficult

to satisfy both of the initial introduction performance of the ink into the printer head (especially into the stacked type printer head) and the prevention of the feathering. *Id.*

As described above, when the recording is performed on the regular paper by using the conventional technique, the following problem has arisen. Application (as filed), ¶ [0013]. That is, all of or any one of the troubles arise, for example, such that the feathering is caused on the recording paper, the ink is insufficiently spread on the recording paper, and any trouble occurs in relation to the initial introduction performance of the ink into the printer head. As a result, it has been impossible to obtain any one which has the satisfactory printing quality.

The present invention has been made in order to solve the problems as described above, an object of which is to provide a water base ink for ink-jet recording which is satisfactory in the initial introduction performance of the ink into an ink flow passage of a printer head mounted on an ink-jet printer, especially of a stacked type printer head, and which does not cause the feathering and the insufficient spread of the ink even when the recording is performed on the regular paper. Application (as filed), ¶ [0014].

Independent Claim 13 is supported by the portions of the specification discussed below. According to a third aspect of the present invention, there is provided a water base ink for ink-jet recording comprising:

- a dispersible coloring agent;
- a propylene glycol ether; and
- a surfactant represented by the following general formula (3).



Application (as filed), ¶ [0023]. Wherein n represents an integer of 2 to 4, R¹ represents an alkyl group having a number of carbon atoms of 12 to 15, and M represents Na or triethanolamine. *Id.*

The water base ink for ink-jet recording according to the third aspect contains the dispersible coloring agent, the propylene glycol ether, and the surfactant represented by the general formula (3). Application (as filed), ¶ [0024]. The propylene glycol ether includes, in its molecular structure, the frame of (CHCH₃CH₂O) which is a lipophilic component. *Id.* Therefore,

even when the amount of addition is small, the permeation into the paper is excellent. *Id.* Thus, it is possible to prevent from the insufficient spread of the ink without affecting the feathering of the ink on the recording paper. *Id.* Further, it is possible to realize the improvement in wettability with respect to the ink flow passage of the printer head and the quick release of bubbles or foams which are generated in the ink flow passage or which are allowed to flow into the ink flow passage to the outside of the ink flow passage without deteriorating the foregoing effect of the propylene glycol ether owing to the surface-active function possessed by the surfactant represented by the general formula (3) described above. *Id.*

According to the present invention, there is also provided an ink cartridge which accommodates each of the inks as defined in the first to third aspects. Application (as filed), ¶ [0025]. The ink cartridge may have, for example, a chamber for accommodating a single color ink or a plurality of chambers for accommodating inks having different colors. *Id.* The ink cartridge may be installed to a head of an ink-jet printer. *Id.* Alternatively, the ink cartridge may be installed to a main body of an ink-jet printer, for example, a case. *Id.*

According to a fourth aspect of the present invention, there is provided an ink-jet printer comprising:

an ink-jet head which has an ink flow passage formed of an Ni alloy and
which discharges an ink; and

an ink cartridge which accommodates the ink as defined in the third aspect of the present invention, the ink being supplied to the ink-jet head. The ink is satisfactory in wettability with respect to the ink flow passage formed of the Ni alloy. Therefore, the initial introduction performance of the ink is excellent. The ink flow passage may be formed in a stack composed of sheets formed of an Ni-Fe alloy.

Application (as filed), ¶ [0026].

6. GROUND OF REJECTION TO BE REVIEWED ON APPEAL

1. Whether claims 13-20 are unpatentable under 35 U.S.C. § 103(a) as being obvious over U.S. Patent Application No. 2003/0195275 to Sanada et al. ("Sanada") in view of JP 2001-081372 to Ikemoto et al. ("Ikemoto").

2. Whether claims 13-18 are unpatentable under 35 U.S.C. § 103(a) as being obvious over U.S. Patent No. 6,485,138 to Kubota et al. ("Kubota") in view of Ikemoto.

7. ARGUMENT

1. *Whether claims 13-20 are unpatentable under 35 U.S.C. § 103(a) as being obvious over U.S. Patent Application No. 2003/0195275 to Sanada et al. ("Sanada") in view of JP 2001-081372 to Ikemoto et al. ("Ikemoto").*

A. **SUMMARY OF RELEVANT LAW**

The determination of obviousness rests on whether the claimed invention as a whole would have been obvious to a person of ordinary skill in the art at the time the invention was made. In determining obviousness, four factors should be weighed: (1) the scope and content of the prior art, (2) the differences between the art and the claims at issue, (3) the level of ordinary skill in the art, and (4) whatever objective evidence may be present. Obviousness may not be established using hindsight or in view of the teachings or suggestions of the inventor. The Examiner carries the burden under 35 U.S.C. § 103 to establish a prima facie case of obviousness and must show that the references relied on teach or suggest all of the limitations of the claims.

B. **SANADA AND IKEMOTO FAIL TO TEACH OR SUGGEST ALL OF THE LIMITATIONS OF THE CLAIMS**

On page 3 of the Final Office Action (11/27/06), the Examiner rejects claims 13-20 under 35 U.S.C. § 103(a) as being unpatentable over Sanada in view of Ikemoto. These rejections are respectfully traversed and believed overcome in view of the following discussion.

(1) **Claim 13**

Independent Claim 13 states:

"A water base ink for ink-jet recording comprising:

"a dispersible coloring agent;

"a proplene-glycol ether;

“a surfactant represented by the following general formula (3):



wherein n represents an integer of 2 to 4, R¹ represents an alkyl group having a number of carbon atoms of 12 to 15, and M represents Na or triethanolamine.”

The Examiner asserts that Sanada discloses a propylene glycol ether at paragraph [0076]. However, the only glycol ethers disclosed by Sanada are ethylene glycol monomethyl (or ethyl) ether, diethylene glycol monomethyl (or ethyl) ether, and triethylene glycol monomethyl (or ethyl) ether. These are all ethylene-glycol ethers. None of them are propylene-glycol ethers. Accordingly, the combination of Sanada and Ikemoto fails to teach or suggest all of the limitations of Claim 13.

The Examiner has failed to address this deficiency of the references in the Examiner’s Advisory Action dated April 10, 2007. As such, Applicants respectfully assert that, for this reason alone, the Examiner has failed to establish a prima facie case of obviousness of independent Claim 13.

In addition, the Examiner admits that Sanada fails to disclose a surfactant represented by the Formula (3) of the current application. Office Action (11/27/06), P. 1. As a result, the Examiner cites to Ikemoto for the disclosure of Formula (3). *Id.* However, the teachings of Ikemoto are directed to an ink containing a non-dispersible coloring agent, i.e., a pigment, while Claim 13 contains a dispersible coloring agent. Non-dispersible coloring agents behave very differently from dispersible coloring agents. Surfactants that work well with non-dispersible coloring agents do not necessarily work well with dispersible coloring agents. In fact, Ikemoto specifically states that the polyoxyethylene alkyl ethereal sulfate derivative disclosed is included solely to disperse the pigment. On the other hand, the surfactants disclosed in Sanada are not included as dispersants as the ink of Sanada contains a self-dispersing pigment. Sanada, P. 2, ¶ [0013]. Moreover, there is no suggestion in either Sanada or Ikemoto that the polyoxyethylene alkyl ethereal sulfate derivative disclosed in Ikemoto is substitutable for the

surfactants disclosed in Sanada. As a result, one of ordinary skill in the art would find (1) no motivation to combine the teachings of Ikemoto with those of Sanada and (2) no reasonable expectation of success of combining the teachings of Ikemoto with those of Sanada.

The Examiner asserts, in the Examiner's Advisory Action, that it is obvious to combine Sanada and Ikemoto because Sanada discloses a self-dispersing pigment and Ikemoto discloses a pigment and a dispersant compound. However, Examiner's logic on this matter is flawed. Ikemoto clearly teaches dispersing a non-dispersible pigment by using a dispersant. Sanada, on the other hand, teaches the use of a self-dispersing pigment. Once the pigment is self-dispersing, there is no need to use a dispersing agent. Therefore, there is no reason to combine the dispersant of Ikemoto with the ink compositions of Sanada. Moreover, even if there were a motivation, which Applicants contend there is not, the combination of the references would still fail to teach all of the elements of Claim 13. In particular, the Examiner asserts that Ikemoto teaches a self-dispersing pigment. Even if this were correct, Ikemoto fails to teach combining a self dispersing pigment with a dispersant. Claim 13 clearly states that the ink has "a dispersible coloring agent" **and** "a surfactant represented by the following general formula (3)". Ikemoto fails to teach or suggest such a combination. Therefore, the Examiner cannot show a motivation to combine "a dispersible coloring agent" with "a surfactant represented by the following general formula (3)", or that there is a reasonable expectation of success of the combination of Ikemoto with Sanada.

Since the references cited by the Examiner (a) fail to teach or suggest a proplene-glycol ether, (b) fail to teach or suggest a dispersible coloring agent and a surfactant represented by the following general formula (3), and (c) there is no motivation to combine the references and no reasonable expectation of success of the combination, Applicants respectfully assert that Examiner has failed to establish a prima facie case of obviousness of independent Claim 13. Therefore, Applicants respectfully request that Examiner remove the rejections of Claim 13 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent Application No. 2003/0195275 to Sanada et al. in view of JP 2001-081372 to Ikemoto et al.

(2) Claim 14

Claim 14 is dependent from Claim 13. As Claim 13 is allowable, so must be Claim 14. In addition, Claim 14 states, in part:

“wherein the propylene glycol ether is dipropylene glycol propyl ether.”

As discussed above, Sanada fails to disclose any propylene glycol ether, let alone dipropylene glycol propyl ether. As a result, the combination of Sanada and Ikemoto fails to teach or suggest all of the limitations of Claim 14.

Since the references cited by the Examiner fail to teach or suggest each and every element as set forth in Claim 14, Applicants respectfully assert that Examiner has failed to establish a prima facie case of obviousness of Claim 14. Therefore, Applicants respectfully request that Examiner remove the rejections of Claim 14 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent Application No. 2003/0195275 to Sanada et al. in view of JP 2001-081372 to Ikemoto et al.

(3) Claim 15

Claim 15 is dependent from Claim 13. As Claim 13 is allowable, so must be Claim 15. In addition, Claim 15 states, in part:

“wherein a content of the propylene glycol ether is 2% by weight to 3% by weight.”

As discussed above, Sanada fails to disclose any propylene glycol ether, let alone the range of propylene glycol ether of Claim 15. As a result, the combination of Sanada and Ikemoto fails to teach or suggest all of the limitations of Claim 15.

Since the references cited by the Examiner fail to teach or suggest each and every element as set forth in Claim 15, Applicants respectfully assert that Examiner has failed to establish a prima facie case of obviousness of Claim 15. Therefore, Applicants respectfully request that Examiner remove the rejections of Claim 15 under 35 U.S.C. § 103(a) as being

unpatentable over U.S. Patent Application No. 2003/0195275 to Sanada et al. in view of JP 2001-081372 to Ikemoto et al.

(4) Claim 16

Claim 16 is dependent from Claim 13. As Claim 13 is allowable, so must be Claim 16. In addition, Claim 16 states, in part:

“wherein the surfactant represented by general formula (3) is contained by 0.1 to 3% by weight.”

As Examiner has admitted, Sanada fails to disclose any surfactant of general formula (3). Yet the Examiner cites to Sanada as disclosing this claim language of Claim 16. This is obviously an impossibility. Since Sanada admittedly fails to disclose general formula (3), it cannot disclose the amount of general formula (3) as specified in Claim 16. As a result, the combination of Sanada and Ikemoto fails to teach or suggest all of the limitations of Claim 16.

Since the references cited by the Examiner fail to teach or suggest each and every element as set forth in Claim 16, Applicants respectfully assert that Examiner has failed to establish a prima facie case of obviousness of Claim 16. Therefore, Applicants respectfully request that Examiner remove the rejections of Claim 16 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent Application No. 2003/0195275 to Sanada et al. in view of JP 2001-081372 to Ikemoto et al.

(5) Claim 17

Claim 17 is dependent from Claim 13. As Claim 13 is allowable, so must be Claim 17. In addition, Claim 17 states, in part:

“wherein a content ratio by weight of propylene glycol ether/surfactant is 5 to 10.”

As Examiner has admitted, Sanada fails to disclose any surfactant of general formula (3). Yet the Examiner cites to Sanada as disclosing this claim language of Claim 17. This is obviously an impossibility. Since Sanada admittedly fails to disclose the surfactant general formula (3) and fails to disclose any propylene glycol ether, it cannot disclose any ratio

between that surfactant and the propylene glycol ether as specified in Claim 17. As a result, the combination of Sanada and Ikemoto fails to teach or suggest all of the limitations of Claim 17.

Since the references cited by the Examiner fail to teach or suggest each and every element as set forth in Claim 17, Applicants respectfully assert that Examiner has failed to establish a prima facie case of obviousness of Claim 17. Therefore, Applicants respectfully request that Examiner remove the rejections of Claim 17 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent Application No. 2003/0195275 to Sanada et al. in view of JP 2001-081372 to Ikemoto et al.

(6) Claims 18-20

Claims 18-20 are ultimately dependent from Claim 13. As Claim 13 is allowable, so must be claims 18-20. Therefore, Applicants respectfully request that Examiner remove the rejections of claims 18-20 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent Application No. 2003/0195275 to Sanada et al. in view of JP 2001-081372 to Ikemoto et al.

2. *Whether claims 13-18 are unpatentable under 35 U.S.C. § 103(a) as being obvious over U.S. Patent No. 6,485,138 to Kubota et al. ("Kubota") in view of JP 2001-081372 to Ikemoto et al. ("Ikemoto").*

A. SUMMARY OF RELEVANT LAW

The determination of obviousness rests on whether the claimed invention as a whole would have been obvious to a person of ordinary skill in the art at the time the invention was made. In determining obviousness, four factors should be weighed: (1) the scope and content of the prior art, (2) the differences between the art and the claims at issue, (3) the level of ordinary skill in the art, and (4) whatever objective evidence may be present. Obviousness may not be established using hindsight or in view of the teachings or suggestions of the inventor. The Examiner carries the burden under 35 U.S.C. § 103 to establish a prima facie case of obviousness and must show that the references relied on teach or suggest all of the limitations of the claims.

B. KUBOTA AND IKEMOTO FAIL TO TEACH OR SUGGEST ALL OF THE LIMITATIONS OF THE CLAIMS

On page 3 of the current Office Action, the Examiner rejects claims 13-18 under 35 U.S.C. § 103(a) as being unpatentable over Kubota in view Ikemoto. This rejection is respectfully traversed and believed overcome in view of the following discussion.

(1) Claim 13

Independent Claim 13 states:

“A water base ink for ink-jet recording comprising:

“a dispersible coloring agent;

“a proplene-glycol ether;

“a surfactant represented by the following general formula (3):



wherein n represents an integer of 2 to 4, R¹ represents an alkyl group having a number of carbon atoms of 12 to 15, and M represents Na or triethanolamine.”

The Examiner asserts that Kubota discloses all of Claim 13 except for the surfactant of general formula (3). However, this misconstrues the teachings of Kubota. Specifically, the Examiner’s interpretation of Kubota ignores the fact that it discloses two types of colorants: dyes and pigments.

Claim 13 requires a dispersible coloring agent. Pigments alone are not dispersible coloring agents. Pigments only become dispersible coloring agents when they are chemically modified to be dispersible. Thus, the only teachings of Kubota that might relate to Claim 13 are those teachings that relate to self dispersing colorant. The teachings of Kubota that relate to non-dispersible pigments are inapplicable to Claim 13.

The Examiner admits that Kubota fails to disclose a surfactant represented by the Formula (3) of the current application. Office Action (11/27/06), P. 1. As a result, the Examiner

cites to Ikemoto for the disclosure of Formula (3). *Id.* However, the teachings of Ikemoto are directed to an ink containing a non-dispersible coloring agent, i.e., a pigment, while Claim 13 contains a dispersible coloring agent. Non-dispersible coloring agents behave very differently from dispersible coloring agents. Surfactants that work well with non-dispersible coloring agents do not necessarily work well with dispersible coloring agents. Therefore, Ikemoto fails to disclose the use of a surfactant represented by Formula (3) with a dispersible coloring agent.

Examiner argues that both Kubota and Ikemoto teach the use of a pigment and a dispersant. Thus, Examiner asserts that it is obvious to combine Kubota and Ikemoto. However, Examiner fails to explain how it is obvious to apply the teachings of Ikemoto which relate to the use of a non-dispersible pigment and a dispersant, to the teachings of Kubota that relate to the use of a dispersible colorant, which does not need a dispersant.

The fact that Ikemoto teaches only to a non-dispersible pigment and a dispersant bears directly on Ikemoto's applicability to Kubota. Kubota, however, teaches both an ink which uses a non-dispersible pigment and a dispersant, and an ink which only uses a dispersible colorant. Since Ikemoto's teachings relate only to the use of a non-dispersible pigment and a dispersant, Ikemoto's teachings do not relate to the use of a dispersible coloring agent. Therefore, as stated earlier, it is not obvious that a compound which is useful as a dispersant for a non-dispersible pigment is also useful as a surfactant along with a dispersible colorant. Moreover, there is no suggestion in either Kubota or Ikemoto that the polyoxyethylene alkyl ethereal sulfate derivative disclosed in Ikemoto is substitutable for the surfactants disclosed in Kubota.

As a result, one of ordinary skill in the art would find (1) no motivation to combine the teachings of Ikemoto that that relate to a non-dispersible pigment and a dispersant, with those of Kubota that relate to a dispersible colorant, and (2) no reasonable expectation of success of combining the teachings of Ikemoto that that relate to a non-dispersible pigment and a dispersant, with those of Kubota that relate to a dispersible colorant.

Since the references cited by the Examiner fail to teach or suggest the use of a surfactant represented by Formula (3) with a dispersible coloring agent as set forth in independent Claim 13, and since there is no motivation to combine the references and no reasonable expectation of success of the combination, Applicants respectfully assert that Examiner has failed to establish a prima facie case of obviousness of independent Claim 13. Therefore, Applicants respectfully request that Examiner remove the rejections of Claim 13 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent No. 6,485,138 to Kubota et al. in view of JP 2001-081372 to Ikemoto et al.

(2) Claim 14

Claim 14 is dependent from Claim 13. As Claim 13 is allowable, so must be Claim 14. In addition, Claim 14 states, in part:

“wherein the propylene glycol ether is dipropylene glycol propyl ether.”

Kubota, however, fails to disclose dipropylene glycol propyl ether specifically. Moreover, Ikemoto also fails to disclose dipropylene glycol propyl ether. As a result, the combination of Kubota and Ikemoto fails to teach or suggest all of the limitations of Claim 14.

Since the references cited by the Examiner fail to teach or suggest each and every element as set forth in Claim 14, Applicants respectfully assert that Examiner has failed to establish a prima facie case of obviousness of Claim 14. Therefore, Applicants respectfully request that Examiner remove the rejections of Claim 14 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent No. 6,485,138 to Kubota et al. in view of JP 2001-081372 to Ikemoto et al..

(3) Claim 15

Claim 15 is dependent from Claim 13. As Claim 13 is allowable, so must be Claim 15. In addition, Claim 15 states, in part:

“wherein a content of the propylene glycol ether is 2% by weight to 3% by weight.”

The Examiner incorrectly relies on the range for the solvent disclosed in Kubota as disclosing the range of propylene glycol ether. Propylene glycol mono-methyl ether and dipropylene glycol mono-methyl ether are never disclosed as solvents in Kubota, they are only disclosed as surfactants. Since no range for the surfactant of Kubota is given, and propylene glycol ether is not disclosed in any of the examples, Kubota completely fails to disclose the range of propylene glycol ether as stated in Claim 15. As a result, the combination of Kubota and Ikemoto fails to teach or suggest all of the limitations of Claim 15.

Since the references cited by the Examiner fail to teach or suggest each and every element as set forth in Claim 15, Applicants respectfully assert that Examiner has failed to establish a prima facie case of obviousness of Claim 15. Therefore, Applicants respectfully request that Examiner remove the rejections of Claim 15 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent No. 6,485,138 to Kubota et al. in view of JP 2001-081372 to Ikemoto et al.

(4) Claim 16

Claim 16 is dependent from Claim 13. As Claim 13 is allowable, so must be Claim 16. In addition, Claim 16 states, in part:

“wherein the surfactant represented by general formula (3) is contained by 0.1 to 3% by weight.”

As Examiner has admitted, Kubota fails to disclose any surfactant of general formula (3). Yet the Examiner cites to Kubota as disclosing this claim language of Claim 16. This is obviously an impossibility. Since Kubota admittedly fails to disclose general formula (3), it cannot disclose the amount of general formula (3) as specified in Claim 16. As a result, the combination of Kubota and Ikemoto fails to teach or suggest all of the limitations of Claim 16.

Since the references cited by the Examiner fail to teach or suggest each and every element as set forth in Claim 16, Applicants respectfully assert that Examiner has failed to establish a prima facie case of obviousness of Claim 16. Therefore, Applicants respectfully request that Examiner remove the rejections of Claim 16 under 35 U.S.C. § 103(a) as being

unpatentable over U.S. Patent No. 6,485,138 to Kubota et al. in view of JP 2001-081372 to Ikemoto et al.

(5) Claim 17

Claim 17 is dependent from Claim 13. As Claim 13 is allowable, so must be Claim 17. In addition, Claim 17 states, in part:

“wherein a content ratio by weight of propylene glycol ether/surfactant is 5 to 10.”

As Examiner has admitted, Kubota fails to disclose any surfactant of general formula (3). Yet the Examiner cites to Kubota as disclosing this claim language of Claim 17. This is obviously an impossibility. Moreover, Kubota completely fails to disclose any range of the amount of propylene glycol ether. Since Kubota admittedly fails to disclose the surfactant general formula (3) and fails to disclose any range of the amount of propylene glycol ether, it cannot disclose any ratio between that surfactant and the propylene glycol ether as specified in Claim 17. As a result, the combination of Kubota and Ikemoto fails to teach or suggest all of the limitations of Claim 17.

Since the references cited by the Examiner fail to teach or suggest each and every element as set forth in Claim 17, Applicants respectfully assert that Examiner has failed to establish a prima facie case of obviousness of Claim 17. Therefore, Applicants respectfully request that Examiner remove the rejections of Claim 17 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent No. 6,485,138 to Kubota et al. in view of JP 2001-081372 to Ikemoto et al.

(6) Claims 18

Claim 18 is ultimately dependent from Claim 13. As Claim 13 is allowable, so must be Claim 18. Therefore, Applicants respectfully request that Examiner remove the rejections of Claim 18 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent No. 6,485,138 to Kubota et al. in view of JP 2001-081372 to Ikemoto et al.

8. CLAIMS APPENDIX

Claims 1-12 (withdrawn)

Claim 13 (original): A water base ink for ink-jet recording comprising:

a dispersible coloring agent;

a propylene glycol ether; and

a surfactant represented by the following general formula (3):



wherein n represents an integer of 2 to 4, R¹ represents an alkyl group having a number of carbon atoms of 12 to 15, and M represents Na or triethanolamine.

Claim 14 (original): The water base ink for ink-jet recording according to claim 13, wherein the propylene glycol ether is dipropylene glycol propyl ether.

Claim 15 (original): The water base ink for ink-jet recording according to claim 13, wherein a content of the propylene glycol ether is 2 % by weight to 3 % by weight.

Claim 16 (original): The water base ink for ink-jet recording according to claim 13, wherein the surfactant represented by the general formula (3) is contained by 0.1 to 3 % by weight.

Claim 17 (original): The water base ink for ink-jet recording according to claim 13, wherein a content ratio by weight of propylene glycol ether/surfactant is 5 to 10.

Claim 18 (original): An ink cartridge comprising the water base ink for ink-jet recording as defined in claim 13.

Claim 19 (original): An ink-jet printer comprising:

an ink-jet head which has an ink flow passage formed of an Ni alloy and which discharges an ink; and

the ink cartridge as defined in claim 18 which accommodates the ink to be supplied to the ink-jet head.

Claim 20 (original): The ink-jet printer according to claim 19, wherein the ink flow passage is formed in a stack composed of sheets formed of an Ni-Fe alloy.

9. EVIDENCE APPENDIX

A copy of U.S. Patent Application No. 2003/0195275 to Sanada et al. has been attached to this Appeal Brief as Exhibit A. A copy of JP 2001-081372 to Ikemoto et al. has been attached to this Appeal Brief as Exhibit B. A copy of U.S. Patent No. 6,485,138 to Kubota et al. has been attached to this Appeal Brief as Exhibit C. Each of the above references was cited to by the Examiner in the Final Office Action mailed on November 27, 2006.

10. **RELATED PROCEEDINGS APPENDIX**

Not applicable.

11. CONCLUSION

In view of the foregoing, it is submitted that the final rejection of the Examiner based on the art of record is improper. Accordingly, it is requested that this Board reverse the Rejection Raised by the Examiner.

Respectfully submitted,

Dated: June 22, 2007

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Appendix A

Appendix B

INK-JET RECORDING INK COMPOSITION AND METHOD FOR PRODUCING THE SAME

Publication number: JP2001081372

Publication date: 2001-03-27

Inventor: IKEMOTO ETSUO; FUKUI MASAYUKI; MORI SHIRO;
KUGE ISHIO

Applicant: FUJI PIGMENT

Classification:

- International: **B41J2/01; B41M5/00; C09D11/00; B41J2/01;
B41M5/00; C09D11/00; (IPC1-7): C09D11/00;
B41J2/01; B41M5/00**

- european:

Application number: JP19990262936 19990917

Priority number(s): JP19990262936 19990917

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Abstract of JP2001081372

PROBLEM TO BE SOLVED: To obtain the subject composition where the fine-particle dispersed system is excellent in long-term preservation stability, stability in a temperature change cycle ranging from a high temperature to freezing, etc., by including pigment, a dispersant composed of a specific derivative and an aqueous medium. **SOLUTION:** The objective composition is obtained by including (A) pigment, (B) a dispersant composed of a polyoxyethylene alkyl ethereal sulfate derivative of the formula: $RO(CH_2CH_2O)_nSO_3M$ (R is a 10-20C alkyl or alkenyl; M is ammonium, organic amines, alkanolamines or an alkali metal; and n is an average polymerization degree of oxyethylene chain and is 2 to 50) and (C) an aqueous medium. The ingredient A used is preferably C.I.Pigment Black 7, C.I.Pigment Red 122, C.I.Pigment Violet 19, aluminum phthalocyanine, C.I.Pigment Blue 15:3, C.I.Pigment Yellow 55, etc.

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最終頁に続く

(54)【発明の名称】 インクジェット記録用インキ組成物およびその製造方法

(57)【要約】

【課題】 本発明は、インクジェット用記録インキに関するもので、特に微粒子分散系の、1年以上にわたっての長期保存安定性および高温から凍結までの温度変化サイクルでの安定性に優れ、印字において鮮やかな色彩彩度を発現し、印字物の耐水性および耐候性に優れ、乾燥固化したインキ成分の再分散性に優れ、なおかつ、自然環境に配慮した記録インキを提供する。

【解決手段】 特定の選択された顔料、分散剤、水性媒体よりなるインクジェット記録用インキ組成物において、これら 3 成分の選択、組合わせによって本課題を解決できる。

【特許請求の範囲】

【請求項1】 顔料、分散剤、水性媒体を必須成分とするインクジェット記録用インキ組成物において、分散剤が下記構造式

【化1】で表されるポリオキシエチレンアルキルエーテル硫酸エステル塩の誘導体であり、式中RがC=10~20のアルキルまたはアルケニル基から選ばれた一種、あるいは二種以上の混合物、Mがアンモニア、有機アミン類、アルカノールアミン類、アルカリ金属から選ばれた一種、あるいは二種以上であることを特徴とするインクジェット記録用インキ組成物。

【化1】 $RO(CH_2CH_2O)_nSO_3M$

(ただしnはオキシエチレン鎖の平均的な重合度であり、2~50の正数である。)

【請求項2】 前記分散剤において、Mがアンモニア、有機アミン類、アルカノールアミン類から選ばれた一種、あるいは二種以上であることを特徴とする、請求項1に記載されたインクジェット記録用インキ組成物。

【請求項3】 前記分散剤において、Rがオレイルまたはラウリル基から選ばれた一種、あるいは二種であることを特徴とする、請求項1、2のいずれかに記載のインクジェット記録用インキ組成物。

【請求項4】 前記分散剤において、nが2~20であることを特徴とする、請求項1から3のいずれかに記載のインクジェット記録用インキ組成物。

【請求項5】 前記顔料が、C.I.ピグメントブラック 7、C.I.ピグメントレッド 122、C.I.ピグメントバイオレット 19、7-メチル-2-ナフトール、C.I.ピグメントブルー 15:3、C.I.ピグメントブルー 15:6、C.I.ピグメントイエロー 55、C.I.ピグメントイエロー 79、C.I.ピグメントイエロー 128、C.I.ピグメントイエロー 139、C.I.ピグメントイエロー 150のいずれかから選ばれた一種、または二種以上の混合物であることを特徴とする、請求項1から4のいずれかに記載のインクジェット記録用インキ組成物。

【請求項6】 分散系における顔料粒子の平均粒子径が0.01~0.3μmの範囲内であることを特徴とする、請求項1から5のいずれかに記載のインクジェット記録用インキ組成物。

【請求項7】 インクジェット記録用インキにバインダー樹脂を含有させる事を特徴とし、前記樹脂が親水性ポリエステル、親水性ウレタン樹脂、あるいはポリビニルアルコールから選ばれた一種、または二種以上であることを特徴とする、請求項1から6のいずれかに記載のインクジェット記録用インキ組成物。

【請求項8】 分散装置として三本ロールミル、または径が0.2~1.5mmのビーズを媒体とした湿式サンドミルを用いることを特徴とする、請求項1から7のいずれかに記載のインクジェット記録用インキ組成物の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、インクジェット記録用インキに関するもので、特にサーマル方式やピエゾ方式などあらゆる印字方式に対応でき、微粒子分散系の、1年以上にわたっての長期保存安定性および高温から凍結までの温度変化サイクルでの安定性に優れ、印字において鮮やかな色彩彩度を発現し、印字物の耐水性および耐候性に優れ、乾燥固化したインキ成分の再分散性に優れ、なおかつ、自然環境に配慮した記録インキに関するものである。

【0002】

【従来の技術】 インクジェット記録方式とは、サーマル方式やピエゾ方式などインクを吐出する機構により色々な方法があるが、いずれの場合においても微細なノズルよりインク液滴を吐出して記録画像を得る方式である。

【0003】 このようなインクジェット記録方式に使用するインキとしては、現在染料を水または親水性有機溶剤との混合系からなる液媒体に溶解して使用されているが、記録物の耐候性や耐水性などの点では不満足である。

【0004】 以上の背景より近年、顔料タイプのインクジェット記録用インキについて開発が行われており、各種顔料と様々な水溶性高分子、分散剤またはこれらの組み合わせによる顔料分散インキが開示されている。

【0005】 使用される顔料として、例えば特開平11-166145、特開平11-131001、特開平2-255875などに、特に限定されることなく、従来公知のものを使用できる旨が記載されている。しかし必要とされる色調、および強い耐候性、この2点を十分に満たした顔料を用いることは当然のことであるが、インクジェット記録用インキに使用される顔料は、液媒体中に微細な粒子で安定に分散することが強く求められている。また、酸化チタン、弁柄などの無機顔料は、たとえ十分微細な粒子として分散させたとしても、その高比重のため長期間の貯蔵において、顔料の沈降凝集が発生することから、インクジェット記録用インキへの適用には不向きである。

【0006】 また、有機顔料は化学反応により合成されるが、その化学組成および反応条件、さらに表面処理の処理条件によりその物性が異なる。有機顔料でインクジェット記録用インキを調製する時、顔料の種類と分散剤の種類の組み合わせ、あるいは分散処理方法により、顔料の微細化や分散安定性に差異が生じるので、それらの単純な組み合わせでは当該インキとして満足すべきインキは得られない。

【0007】 分散剤として、例えば特開平5-247393や、特開平8-73790にナトリウム塩中和の水溶性高分子を使用したインクジェット記録用インキの実施例が記載されている。特開平4-227669の例などからも明らかなように、サーマルタイプのインクジェット記録方式では、アルカリ金属塩がインキ吐出口焦げ

付きの原因となることがあり、使用にあたって注意が必要である。また他の例として特開平8-20738、特開平8-41394等のような水溶性樹脂を分散剤としたインキ組成物では、ピエゾ方式では問題はないがサーマル方式を採用した場合、インキ吐出時に樹脂の焦げ付きが起こり、ノズルの目詰まりを発生させる。すなわち、樹脂系分散剤には問題点が多いのである。

【0008】一方、界面活性剤を分散剤として使用したインキ組成物も各種提案されており例えば特開平8-199100、特開平10-279869、特開平11-116872、特開平11-124527などに親水部としてカルボン酸塩、スルホン酸塩、リン酸塩等の陰イオン性塩やポリオキシアルキレン基等のノニオン性置換基を有するものが挙げられている。しかし、分散剤の置換基を選択しただけでは満足すべきインクジェット記録用インキ組成物が得られるわけではない。置換基の選択もさることながら、インクジェット記録用インキにおいては、微細で長期に安定な顔料の分散を実施するために、顔料と分散剤の組み合わせを巧みに選択することが必要である。

【0009】顔料分散の方法として、各公報にボールミル、アトライター、超音波ホモジナイザーおよびコロイドミルに代表される湿式分散の手法が例示されているが、これら手法では顔料の、サブミクロンへの微細な分散が困難なため、初期的には良好な分散状態が得られるが長期保存すると顔料粒子の沈降や凝集が起こり、結果としてノズルの目詰りが起こるのは明らかである。また、印字物の着色濃度は分散系の顔料粒子径に起因し、粒径が小さいほど着色濃度は高くなる。サブミクロンへの分散は必須事項ではあるが、たとえ最適な分散機を選んだとしても、顔料と分散剤の組み合わせがふさわしくなければ長期に安定な微分散体を得ることが出来ない。

【0010】さらに、プリンターの使用環境やプリンターあるいは補充用インキ輸送時において70℃近くや氷点下で凍結してしまう温度になることがあり、特に凝固点が高く凍結しやすい水性のインキとしては、解凍後の分散性も必要とされる。また、インキ吐出終了後、ノズル上に残ったインキが乾燥固化することがある。これが再溶解しなければノズルの目詰まりの原因となるため、乾燥固化したインキ成分の再分散性も必要である。

【0011】ところで近年米国で出版された“*Our Stolen Future* (邦訳版：奪われし未来)”の主張に代表されるように、「合成化学物質の中に生体が持つホルモンと類似の作用をする物質があり、これが野生動物やヒトの内分泌(ホルモン)作用をかく乱するため、野生動物に起こっている深刻な影響が人間にも及んでいる」という、いわゆる「環境ホルモン問題(またはエンドクリン問題)」がクローズアップされている。

【0012】界面活性剤の分野においても例外なく前記問題が取りざたされており、界面活性剤原料の一種であ

るノニルフェノールに代表される「アルキルフェノール」がその物質として取り上げられている。これを使用して生産されるノニオン活性剤の一種であるアルキルフェノールエトキシレートが環境中に残存した場合、生分解の過程でアルキルフェノールを生成することが知られており、また、前記原料を使用して生産された活性剤の不純物としてアルキルフェノールが微量ながらも残存する。また、これら界面活性剤を顔料分散剤として使用することにあたって、若干ではあるが微分散の能力は弱いものである。

【0013】以上の事項より、非アルキルフェノール系活性剤を使用した分散系の開発は今後における重要課題のひとつである。

【0014】以前、我々は特開平8-199100においてポリオキシエチレンエーテル硫酸エステル塩誘導体を分散剤として使用することを特徴とする旨の特許出願を行った。上記出願では、それ以前の技術と比較して分散剤を特定のものを選択することで改善がなされたのであるが、引き続き顔料と分散剤の組み合わせを中心に検討しているうちに、顔料が微細で、長期に安定な分散を実施するには、それらの特定の組み合わせで格段の効果が発揮する場合を見出し、本発明に至った。

【0015】

【発明が解決しようとする課題】本発明は、従来の欠点を解決するにあたり、微粒子分散系の、1年以上にわたっての長期保存安定性、高温から凍結までの温度変化サイクルでの安定性に優れ、印字において鮮やかな色彩彩度を発現し、印字物の耐水性および耐候性に優れ、乾燥固化したインキ成分の再分散性に優れ、なおかつ、自然環境に配慮した記録インキを提供しようとするものである。

【0016】

【課題を解決するための手段】本発明の記録液は、顔料、分散剤、水性媒体を必須成分とするインクジェット記録用インキ組成物において、前記分散剤が下記構造式

【化1】で表されるポリオキシエチレンエーテル硫酸エステル塩であり、式中RはC=10~20のアルキルまたはアルケニル基から選ばれた一種、あるいは二種以上の混合物であり、Mはアンモニア、有機アミン類、アルコールアミン類、アルカリ金属から選ばれた一種、あるいは二種以上の混合物であることを特徴とするインキ組成物であり、分散剤の高度な選択や、顔料との選択組み合わせ等によって、本課題を解決しようとするものである。

【化1】 $RO(CH_2CH_2O)_nSO_3M$

(ただしnはオキシエチレン鎖の平均的な重合度であり、2~50の正数である。)

【0017】本発明に使用されるポリオキシエチレンアルキルエーテル硫酸エステル塩については、構造式中Rの炭素鎖が10~20のアルキルまたはアルケニルが好ましく、特にオレイル基あるいはラウリル基である場合が、

顔料の微分散における効果が大きい、より好ましい。Rが20より大きくなると水性媒体への溶解度が低下するため、本系への適用にはふさわしくなく、10より小さくなると炭化水素基の、顔料への吸着が弱くなるため、分散系の長期安定化が困難となる。これらは、100%純度である必要は無く、主成分がオレイル、またはラウリルであればよい。nは2~50であることが好ましく、特に好ましいのはnが2~20の場合である。nが50より大きくなると、インキ組成物の粘度が極端に高くなり、吐出性能が悪くなる。また2より小さい場合、長期にわたって安定な顔料の微分散体を得ることが不可能である。以上の範囲で本発明は実施可能であるが、分散能力とインキ粘度の関係から、nが2~20の場合が特に好ましい。また、式中Mはアンモニア、当該硫酸塩が水性媒体に溶解しうる有機アミン類やアルカノールアミン類、あるいはアルカリ金属の場合で実施可能である。しかし先に触れたようにヘッドの焦げ付きの問題より、Mがアンモニア、有機アミン類、アルカノールアミン類である場合が特に好ましく、例えばメチルアミン、エチルアミン、モノエタノールアミン、ジエタノールアミン、トリエタノールアミンが挙げられる。

【0018】本発明に使用される分散剤の使用割合は、顔料の種類や銘柄によっても異なるため、一概に規定できるものではないが、顔料100重量部に対して10~100重量部の範囲で使用可能であるが、インキ粘度に与える影響を考慮すると、10~50重量部の範囲で使用するがより好ましい。

【0019】本発明に使用される水性媒体とは、水または水と親水性有機溶剤の混合物であり、ノズル上におけるインキの保湿効果を目的としたものである。使用可能な親水性有機溶剤としてはエチレングリコール、ジエチレングリコール、トリエチレングリコール、グリセリン、1,3-ブチレングリコールなどの多価アルコール類、エチレングリコールジメチルエーテル、エチレングリコールモノメチルエーテル、トリエチレングリコールモノメチルエーテル、エチレングリコールモノブチルエーテル、トリエチレングリコールモノブチルエーテル等のグリコールエーテル類が挙げられる。これらの親水性有機溶剤は混合して使用しても良い。記録液中に占める重量割合としては5~50重量%である場合が好ましく、特に好ましいのは、5~30重量%の範囲である。親水性有機溶剤が50重量%を超えると、インキ粘度が高くなるため、吐出性能が悪くなる。また、5重量%より少ない場合は、インクカートリッジのヘッドにおける乾燥が速く、ノズルの目詰まりを起こす場合がある。また、水の純度について一般的な水道水のレベルであれば特に問題はないが、アルカリ金属イオンに起因するトラブルを避けるために、イオン交換水であることがより好ましい。

【0020】前記親水性有機溶剤において、N,N-ジメチルホルムアミド、ジメチルスルホキシドに代表される

非プロトン性極性溶媒には顔料溶解力を有するものがあり、これらを水性媒体に使用すると印字物の耐水性および耐候性が低下する恐れがあるため、好ましいものではない。

【0021】本発明で使用される顔料はC.I.ピグメントブラック 7、C.I.ピグメントレッド 122、C.I.ピグメントバイオレット 19、フマルキナクリドン、C.I.ピグメントブルー 15:3、C.I.ピグメントブルー 15:6、C.I.ピグメントイエロー 55、C.I.ピグメントイエロー 79、C.I.ピグメントイエロー 128、C.I.ピグメントイエロー 139、C.I.ピグメントイエロー 150のいずれか、あるいはそれらの混合物である。インキ組成物の着色剤として顔料を用いること自体公知ではあるが、印字において鮮やかな色彩彩度を長期にわたって安定に発現させるためには、最適な色調かつ耐候性のある顔料を、低粘度で長期にわたって微細で安定に分散させることが重要である。以上の事項を念頭において顔料種の検討を行ったところ、前記顔料が特に好ましく、これらの顔料と、選択された特定の親水性有機溶剤、特定の分散剤を、特定割合で組み合わせることによって、インクジェット記録用インキ組成物として最適なものを得ることが可能となった。前記顔料は一般に単独で用いられるが、色調によっては混合物としてもよい。

【0022】本発明の記録用インキ組成物に使用される顔料の使用割合は、印字物に十分な着色濃度を与える濃度であればいずれの濃度でもよいが、インキ組成物中で1~20重量%を占める割合が好ましく、1~10重量%の場合が特に好ましい。顔料の使用割合が20重量%を超えると、インキ粘度が高くなるため、ノズルからのインキ吐出能が悪くなり、1重量%より少ない場合は印字物に十分な着色濃度を与えない。

【0023】本発明の記録用インキ組成物における分散顔料の平均粒子径は0.01~0.3 μ mであることが好ましい。平均粒子径が0.3 μ mより大きくなると、印字物の色濃度が薄くなり、鮮やかな色彩彩度を発現できず、また、初期的には良好な分散状態であっても長期保存すると顔料粒子の沈降が起こり、結果としてノズルの目詰りが起こる。

【0024】本発明の記録用インキ組成物は一般コピー紙などの普通紙に適用するには十分な性能を有しているが、表面処理されたカラープリンター用専用紙に適用した場合は印字物の耐水性及び接着性が不十分である。そこでこれら特殊紙用にバインダー樹脂を添加し、前述の欠点を改良することが可能である。印字性能およびノズルの焦げ付きがなく、分散を破壊しない樹脂を探索した結果、親水性ポリエステル、親水性ウレタン樹脂、あるいはポリビニルアルコールが当該目的にかなうことがわかった。また、水性インキのバインダーとして一般的なアクリル樹脂に代表されるポリカルボン酸類はヘッドの焦げ付きが起こるため、本発明においては不适当である。

【0025】以上、本発明の構成成分について述べてきたが、必要に応じてpH調整剤、防腐剤、キレート化剤等の各種添加剤を加えてもよい。

【0026】本発明に用いられる、径が0.2~1.5 mmのビーズを媒体とした湿式サンドミルとは、細長いベッセルにディスクを複数取りつけた回転軸を挿入し、ベッセル中の分散媒体を高速度で原料液と共に回転攪拌し、分散させる機構である。ビーズ径が1.5 mmより大きくなると顔料の粉碎能力が大きく低下し、平均粒子径が0.3 μm以下の微分散が困難である。これらビーズミルの例として、一般に市販されているダイノミル、スパイクミル、グレンミル等の分散機が挙げられる。

【0027】前記分散機で使用されるビーズの材質としては、例えばガラス、ジルコニア、ジルコン、チタニア、アルミナ等が挙げられるが、特に好ましいのはジルコニア、ジルコン、チタニア、アルミナ等のセラミックビーズである。これらは非常に硬度が高いため、ビーズの磨耗が少なく、また高比重であることも合わさって分散系における顔料の微細化に最適である。媒体としてガラスビーズを用いた場合でも顔料の微細化には問題ないが、ビーズが磨耗しやすくなる。

【0028】さらに、三本ロールミル、径が0.2~1.5 mmのビーズを媒体とした湿式サンドミルにて製造した記録液は、分散機の磨耗に起因する不純物、粗粒子の除去など、必要に応じて遠心分離、濾過等の操作によって記録液を精製しても良い。

【0029】以上、本発明の構成成分、および製法について述べてきた。分散能力が高い分散剤によって、最適な色調を有し、耐候性に優れた微粉碎可能な特定の顔料を、顔料を溶解する恐れのない親水性媒体に、最適な分散機を用いて、平均粒子径が0.01~0.3 μmの微粒子に分散する。以上の事柄を組み合わせる事によって初めて、1年以上にわたっての長期保存安定性および高温から凍結までの温度変化サイクルでの安定性に優れ、印字物に最適な色調、耐候性を与え、乾燥固化したインキ成分の再分散性に優れ、なおかつ自然環境に配慮したインクジェット用記録インキ組成物を提供することができる。以上の要件のうち、1つでも欠如すると本発明における課題を解決する事ができない。必須成分のうち、例えば分散剤を替えると、長期にわたっての安定な微分散が得られず、顔料を替えた場合でも同様のことが当てはまる。分散系の顔料粒子径が0.3 μmより大きくなるとノズルの目詰まり、印字物の色濃度の低下を招くので不適当である。

【0030】以下、本発明において実施例を挙げて説明する。なお、文中にて「部」とあるのは、特に断りのない限り重量基準である。

【0031】得られたインキ組成物の試験方法として、分散系における顔料平均粒子径の測定は、レーザードップラー/周波数解析式粒度分析計（商品名 マイクロト

ラックUPA150、日機装(株)製)にて行った。インキ吐出試験は、各インキ組成物をサーマル方式については、ヒューレット・パカード社製インクカートリッジに充填し、ピエゾ方式については、セイコーエプソン株式会社製インクカートリッジに充填してインキが吐出する事を確認し、そのインキを60℃で12時間、-20℃で12時間放置を7サイクル行う熱サイクル試験を行った後に、顕微鏡で分散状態の確認とインクカートリッジに充填してインキ吐出の可否を調べた。乾燥固化したインキ組成物の再分散性試験は、インキ組成物を130℃乾燥機にて乾燥固化させたものに、水性媒体を添加、攪拌して溶解した後の粒度分布変化を観察した。なお、実施例中、分散剤のカッコ内はオキシエチレン鎖の平均的な重合度である。

【0032】

【実施例1】

顔料 : C.I. ピグメントブラック7

50.0 部

分散剤 : ポリオキシエチレン(12)

20 ラウリルエーテル硫酸アンモニウム

15.0 部

保湿剤 : ジエチレングリコール

15.0 部

水

30.0 部

防腐剤 (商品名プロクセルGXL ZENECA製)

2.0 部

pH調整剤 : ジエタノールアミン

2.0 部

30 上記成分を混合した後、三本ロールミルにて分散処理を行い、顔料分散液を得た。

その顔料分散液に、

保湿剤 : グリセリン

150.0 部

水

736.0 部

を加え混合攪拌した後、これを遠心分離にかけて粗粒子を取り除き、顔料分4.6%、分散系中の顔料平均粒子径が0.08 μmであるインクジェット記録用インキを得

40 た。このインキをインクカートリッジに充填し、印字試験を行ったところ良好な印字物が得られ、熱サイクル試験を行った後も顔料粒子の凝集は見られず、再度印字試験を行ったがサイクル試験前と変わらぬ吐出性能であった。また、再分散性試験後の顔料平均粒子径にも変化はなかった。

【0033】

【比較例1】 実施例1における分散剤をポリオキシエチレン(5)ラウリルエーテル(商品名 エマルゲン 106、花王(株)製)に替えた以外は実施例1と同様にし

60 て、分散系中の顔料平均粒子径が0.09 μmであるイン

クジェット記録用インキを得た。このインキをインクカートリッジに充填し、印字試験を行ったところ良好な印字物が得られたが、熱サイクル試験を行った後、顔料粒子の凝集がみられ、再度印字試験を行ったが印字不能であった。

【0034】

【実施例2】

顔料 : C. I. ピグメントエロー 55

30.0 部

分散剤 : ポリオキシエチレン(18)

オレイルエーテル硫酸アンモニウム

8.0 部

保湿剤 : グリセリン

165.0 部

水

793.0 部

防腐剤 (商品名プロクセルGXL)

2.0 部

pH調整剤 : アンモニア

2.0 部

上記成分を混合した後、径が0.5~0.8 mmのビーズを媒体とした湿式サンドミルにて分散処理を行った後、遠心分離にかけて粗粒子を取り除き、顔料分2.9%、分散系中の顔料平均粒子径が0.15 μm であるインクジェット記録用インキを得た。このインキをインクカートリッジに充填し、印字試験を行ったところ良好な印字物が得られ、熱サイクル試験を行った後も顔料粒子の凝集は見られず、再度印字試験を行ったがサイクル試験前と変わらぬ吐出性能であった。また、再分散性試験後の顔料平均粒子径にも変化はなかった。

【0035】

【比較例2】実施例2における分散機をボールミルに替えて分散処理を行った以外は実施例2と同様にしてインクジェット記録用インキを得たが、分散系中の顔料平均粒子径が1.5 μm と大きく、このインキをインクカートリッジに充填し、印字試験を行ったところ印字物の着色濃度が薄く、また初期的には良好な印字であったが、やがてカスレが発生し、最終的に印字不能となった。

【0036】

【実施例3】

顔料 : C. I. ピグメントバイオレット19

40.0 部

分散剤 : ポリオキシエチレン(3)

アルキルエーテル硫酸トリエタノールアミン

10.0 部

保湿剤 : エチレングリコール

15.0 部

水

30.0 部

防腐剤 (商品名プロクセルGXL ZENECA製)

2.0 部

上記成分を混合した後、三本ロールミルにて分散処理を行い、顔料分散液を得た。その顔料分散液に

保湿剤 : ジエチレングリコール

200.0 部

水

703.0 部

を加え混合攪拌した後、これを遠心分離にかけて粗粒子を取り除き、顔料分3.8%、分散系中の顔料平均粒子径

10 が0.15 μm であるインクジェット記録用インキを得

た。このインキをインクカートリッジに充填し、印字試験を行ったところ良好な印字物が得られ、熱サイクル試験を行った後も顔料粒子の凝集は見られず、再度印字試験を行ったがサイクル試験前と変わらぬ吐出性能であった。また、再分散性試験後の顔料平均粒子径にも変化はなかった。

【0037】

【比較例3】実施例3における分散剤をポリオキシエチレン(13) セチルエーテル (商品名エマルゲン 220、

20 花王(株)製) に替えた以外は実施例3と同様にして、分散系中の顔料平均粒子径が0.15 μm であるインクジェット記録用インキを得た。このインキをインクカートリッジに充填し、印字試験を行ったところ良好な印字物が得られたが、熱サイクル試験を行った後、顔料粒子の凝集がみられ、再度印字試験を行ったが印字不能であった。

【0038】

【実施例4】

顔料 : C. I. ピグメントブルー15:3

30 25.0 部

分散剤 : ポリオキシエチレン(5)

ラウリルエーテル硫酸アンモニウム

5.0 部

保湿剤 : グリセリン

200.0 部

保湿剤 : トリエチレングリコール

50.0 部

水

816.0 部

40 防腐剤 (商品名プロクセルGXL)

2.0 部

pH調整剤 : モノエタノールアミン

2.0 部

上記成分を混合した後、径が0.8~1.0 mmのビーズを媒体とした湿式サンドミルにて分散処理を行った後、これを遠心分離にかけて粗粒子を取り除き、顔料分2.4

%、分散系中の顔料平均粒子径が0.10 μm であるインクジェット記録用インキを得た。このインキをインクカートリッジに充填し、印字試験を行ったところ良好な印

50 字物が得られ、熱サイクル試験を行った後も顔料粒子の

凝集は見られず、再度印字試験を行ったがサイクル試験前と変わらぬ吐出性能であった。また、再分散性試験後の顔料平均粒子径にも変化はなかった。

【0039】

【比較例4】実施例4における分散機を、径が1.5~2.0 mmのビーズを媒体とした湿式サンドミルに替えた以外は実施例4と同様にしてインクジェット記録用インキを得たが、分散系中の顔料平均粒子径が0.6 μm と大きく、このインキをインクカートリッジに充填し、印字試験を行ったところ印字物の着色濃度が薄く、また初期的には良好な印字であったが、やがてカスレが発生し、最終的に印字不能となった。

【0040】

【実施例5】

C. I. ピグメントレッド122

40.0 部

分散剤：ポリオキシエチレン(18)

オレイルエーテル硫酸アンモニウム

8.0 部

保湿剤：グリセリン

15.0 部

水

30.0 部

防腐剤（商品名プロクセルGXL）

2.0 部

上記成分を混合した後、三本ロールミルにて分散処理を行い、顔料分散液を得た。その顔料分散液に

保湿剤：ジエチレングリコール

150.0 部

樹脂：ポリウレタン樹脂

（商品名Neorez R-9649 有効成分 34%、アビシア(株)製）

10.0 部

水

745.0 部

を加え混合攪拌した後、これを遠心分離にかけて粗粒子を取り除き、顔料分3.9%、分散系中の顔料平均粒子径が0.12 μm であるインクジェット記録用インキを得た。このインキをインクカートリッジに充填し、印字試験を行ったところ良好な印字物が得られ、熱サイクル試験を行った後も顔料粒子の凝集は見られず、再度印字試験を行ったがサイクル試験前と変わらぬ吐出性能であった。また、再分散性試験後の顔料平均粒子径にも変化はなかった。

【0041】

【比較例5】実施例5における分散剤をポリオキシエチレンオレイルエーテル（商品名 エマルゲン 420 花王(株)製）に替えた以外は実施例5と同様にして、分散系中の顔料平均粒子径が0.14 μm であるインクジェット記録用インキを得た。このインキをインクカートリ

ッジに充填し、印字試験を行ったところ良好な印字物が得られたが、熱サイクル試験を行った後、顔料粒子の凝集がみられ、再度印字試験を行ったが印字不能であった。

【0042】

【実施例6】

顔料：C. I. ピグメントイエロー128

40.0 部

分散剤：ポリオキシエチレン(12)

10 ラウリルエーテル硫酸アンモニウム

15.0 部

保湿剤：グリセリン

100.0 部

保湿剤：1, 3-ブチレングリコール

50.0 部

水

783.0 部

樹脂：ポリエステル樹脂

（商品名プラスコートRZ-105 有効成分 35%、互応化学(株)製）

20 10.0 部

防腐剤（商品名プロクセルGXL）

2.0 部

上記成分を混合した後、径が0.3~0.5 mmのビーズを媒体とした湿式サンドミルにて分散処理を行った後、これを遠心分離にかけて粗粒子を取り除き、顔料分3.9%、分散系中の顔料平均粒子径が0.22 μm であるインクジェット記録用インキを得た。このインキをインクカートリッジに充填し、印字試験を行ったところ良好な印字物が得られ、熱サイクル試験を行った後も顔料粒子の凝集は見られず、再度印字試験を行ったがサイクル試験前と変わらぬ吐出性能であった。また、再分散性試験後の顔料平均粒子径にも変化はなかった。

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【0043】

【比較例6】実施例6における樹脂をアクリル樹脂（商品名 ジョンクリ7001 有効成分 42%ジョンソンポリマー製）に替えた以外は実施例6と同様にして、分散系中の顔料平均粒子径が0.24 μm であるインクジェット記録用インキを得た。このインキは熱サイクル試験、再分散性試験については良好であったが、インクカートリッジに充填して印字試験を行ったところ、印字不能であった。

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【0044】

【実施例7】実施例1から6で得られたインキ組成物を、50℃恒温器中で1年間静置した後、粒度分布変化の観察および印字試験を行ったが、粒度分布に変化はなく、印字試験においても良好な印字物が得られた。

【0045】

【発明の効果】以上に述べた通り、本発明において、1年以上にわたっての長期保存安定性および高温から凍結

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までの温度変化サイクルでの安定性に優れ、印字において鮮やかな色彩彩度を発現し、印字物の耐水性および耐候性に優れ、乾燥固化したインキ成分の再分散性に優

【手続補正書】

【提出日】平成12年2月25日（2000. 2. 25）

【手続補正1】

【補正対象書類名】明細書

【補正対象項目名】請求項1

【補正方法】変更

【補正内容】

【請求項1】 顔料、分散剤、水性媒体を必須成分とするインクジェット記録用インキ組成物において、分散剤が下記構造式

【化1】で表されるポリオキシエチレンアルキルエーテル硫酸エステル塩の誘導体であり、式中RがC=10～20のアルキルまたはアルケニル基から選ばれた一種、あるいは二種以上の混合物、Mがアンモニア、有機アミン類、アルカノールアミン類、アルカリ金属から選ばれた一種、あるいは二種以上であることを特徴とするインクジェット記録用インキ組成物。

【化1】 $RO(CH_2CH_2O)_nSO_3M$

（ただしnはオキシエチレン鎖の平均的な重合度であり、2～50の正数である）

【手続補正2】

【補正対象書類名】明細書

【補正対象項目名】請求項5

【補正方法】変更

【補正内容】

【請求項5】 前記顔料が、C.I.ピグメントブラック 7、C.I.ピグメントレッド 122、C.I.ピグメントバイオレット 19、アミンウムフタロシアニン、C.I.ピグメントブルー 15:3、C.I.ピグメントブルー15:6、C.I.ピグメントイエロー 55、C.I.ピグメントイエロー 79、C.I.ピグメントイエロー 128、C.I.ピグメントイエロー 138、C.I.ピグメントイエロー 150のいずれかから選ばれた一種、または二種以上の混合物であることを特徴とする、請求項1から4のいずれかに記載のインクジェット記録用インキ組成物

【手続補正3】

【補正対象書類名】明細書

【補正対象項目名】0016

【補正方法】変更

【補正内容】

【0016】

【発明を解決するための手段】本発明の記録液は、顔料、分散剤、水性媒体を必須成分とするインクジェット記録用インキ組成物において、分散剤が下記構造式

【化1】で表されるポリオキシエチレンアルキルエーテル硫酸エステル塩の誘導体であり、式中RがC=10～2

0のアルキルまたはアルケニル基から選ばれた一種、あるいは二種以上の混合物、Mがアンモニア、有機アミン類、アルカノールアミン類、アルカリ金属から選ばれた一種、あるいは二種以上であることを特徴とするインクジェット記録用インキ組成物であり、分散剤の高度な選択や、顔料との選択組み合わせ等によって、本課題を解決しようとするものである。

【化1】 $RO(CH_2CH_2O)_nSO_3M$
（ただしnはオキシエチレン鎖の平均的な重合度であり、2～50の正数である）

【化1】 $RO(CH_2CH_2O)_nSO_3M$

（ただしnはオキシエチレン鎖の平均的な重合度であり、2～50の正数である）

【手続補正4】

【補正対象書類名】明細書

【補正対象項目名】0017

【補正方法】変更

【補正内容】

【0017】本発明に使用されるポリオキシエチレンアルキルエーテル硫酸エステル塩については、構造式中Rの炭素鎖が10～20のアルキルまたはアルケニルが好ましく、特にオレイル基あるいはラウリル基である場合が、顔料の微分散における効果が大きいため、より好ましい。Rが20より大きくなると水性媒体への溶解度が低下するため、本系への適用にはふさわしくなく、10より小さくなると炭化水素基の、顔料への吸着が弱くなるため、分散系の長期安定化が困難となる。これらは、100%純度である必要はなく、主成分がC=10～20のアルキルまたはアルケニル基を有するものであればよい。nは2～50であることが好ましく、特に好ましいのはnが2～20の場合である。nが50より大きくなると、インキ組成物の粘度が極端に高くなり、吐出性能が悪くなる。また、2より小さい場合、長期にわたって安定な顔料の微分散体を得ることが不可能である。以上の範囲で本発明は実施可能であるが、分散能力とインキ粘度の関係から、nが2～20の場合が特に好ましい。また、式中Mはアンモニア、当該硫酸塩が水性媒体に溶解しうる有機アミン類やアルカノールアミン類、あるいはアルカリ金属の場合で実施可能である。しかし先に触れたようにヘッドの焦げ付きの問題より、Mがアンモニア、有機アミン類、アルカノールアミン類である場合が特に好ましく、例えばメチルアミン、エチルアミン、モノエタノールアミン、ジエタノールアミン、トリエタノールアミンが挙げられる。

【手続補正5】

【補正対象書類名】明細書

【補正対象項目名】0021

【補正方法】変更

【補正内容】

【0021】本発明で使用される顔料は、C.I.ピグメント7、C.I.ピグメントレッド122、C.I.ピグメントバイオレット19、アルミニウムフタロシアニン、C.I.ピグメントブルー15:3、C.I.ピグメントブルー15:6、C.I.ピグメントイエロー55、C.I.ピグメントイエロー79、C.I.ピグメントイエロー128、C.I.ピグメントイエロー138、C.I.ピグメントイエロー150のいずれかから選ばれた一種、または二種以上の混合物である。インキ組成物の着色剤として顔料を使用すること自体公知ではあるが、印字において鮮

やかな色彩彩度を長期にわたって安定に発現させるためには、最適な色調かつ耐候性のある顔料を、低粘度で長期にわたって微細で安定に分散させることが重要である。以上の事項を念頭において顔料種の検討を行ったところ、前記顔料が特に好ましく、これらの顔料と選択された特定の親水性有機溶剤、特定の分散剤を、特定割合で組み合わせることによって、インクジェット記録用インキ組成物として最適なものを得ることが可能となった。前記顔料は一般に単独で用いられるが、色調によっては混合物としてもよい。

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 2H086 BA53 BA55 BA59 BA60
 4J039 AD06 AE04 AE06 AE07 BA29
 BC07 BC09 BC12 BC13 BC33
 BC54 BC60 BE01 BE12 BE22
 CA06 DA02 DA05 DA08 EA15
 EA16 EA17 EA19 EA21 EA34
 EA38 EA41 EA42 EA44 EA45
 EA46 GA24

Appendix C



US006485138B1

(12) **United States Patent**
Kubota et al.

(10) **Patent No.:** **US 6,485,138 B1**
(45) **Date of Patent:** **Nov. 26, 2002**

(54) **INK JET RECORDING INK AND
RECORDING METHOD**

(75) **Inventors:** **Kazuhide Kubota; Kazuaki
Watanabe; Kiyohiko Takemoto;
Toshiyuki Miyabayashi, all of Suwa
(JP)**

(73) **Assignee:** **Seiko Epson Corporation, Tokyo (JP)**

(*) **Notice:** Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 0 days.

(21) **Appl. No.:** **09/281,417**

(22) **Filed:** **Mar. 30, 1999**

Related U.S. Application Data

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1997.

(30) **Foreign Application Priority Data**

Feb. 22, 1996 (JP) 8-35249

(51) **Int. Cl.⁷** **B41J 2/17**

(52) **U.S. Cl.** **347/96; 347/100**

(58) **Field of Search** **347/96, 100; 428/195;
106/31.58**

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Primary Examiner—John Barlow

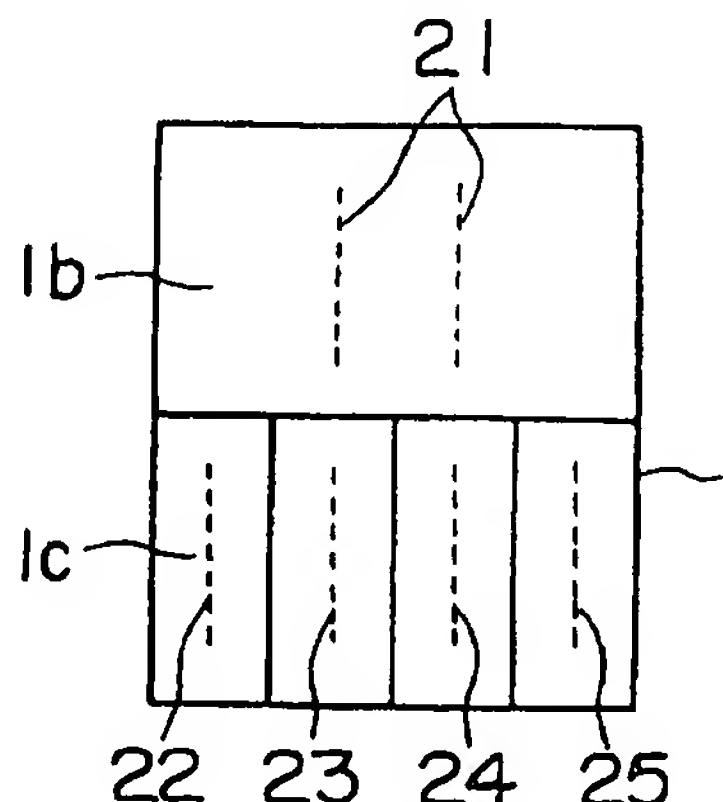
Assistant Examiner—Manish S. Shah

(74) *Attorney, Agent, or Firm*—Ladas & Parry

(57) **ABSTRACT**

An ink jet recording method comprising the step of printing two solutions of a first solution and an ink composition is provided which, even in the case of printing on a recycled paper, can realize a good printed image, especially an image having no significant feathering and free from unevenness of printing and an image free from color bleeding. A first solution containing a polyvalent metal salt and/or a polyalylamine is used in combination with an ink composition containing an inorganic oxide colloid, and optionally an epoxy-containing compound. Specifically, the first solution is deposited onto a recording medium, and the ink composition is then deposited by ink jet printing to perform printing.

9 Claims, 3 Drawing Sheets



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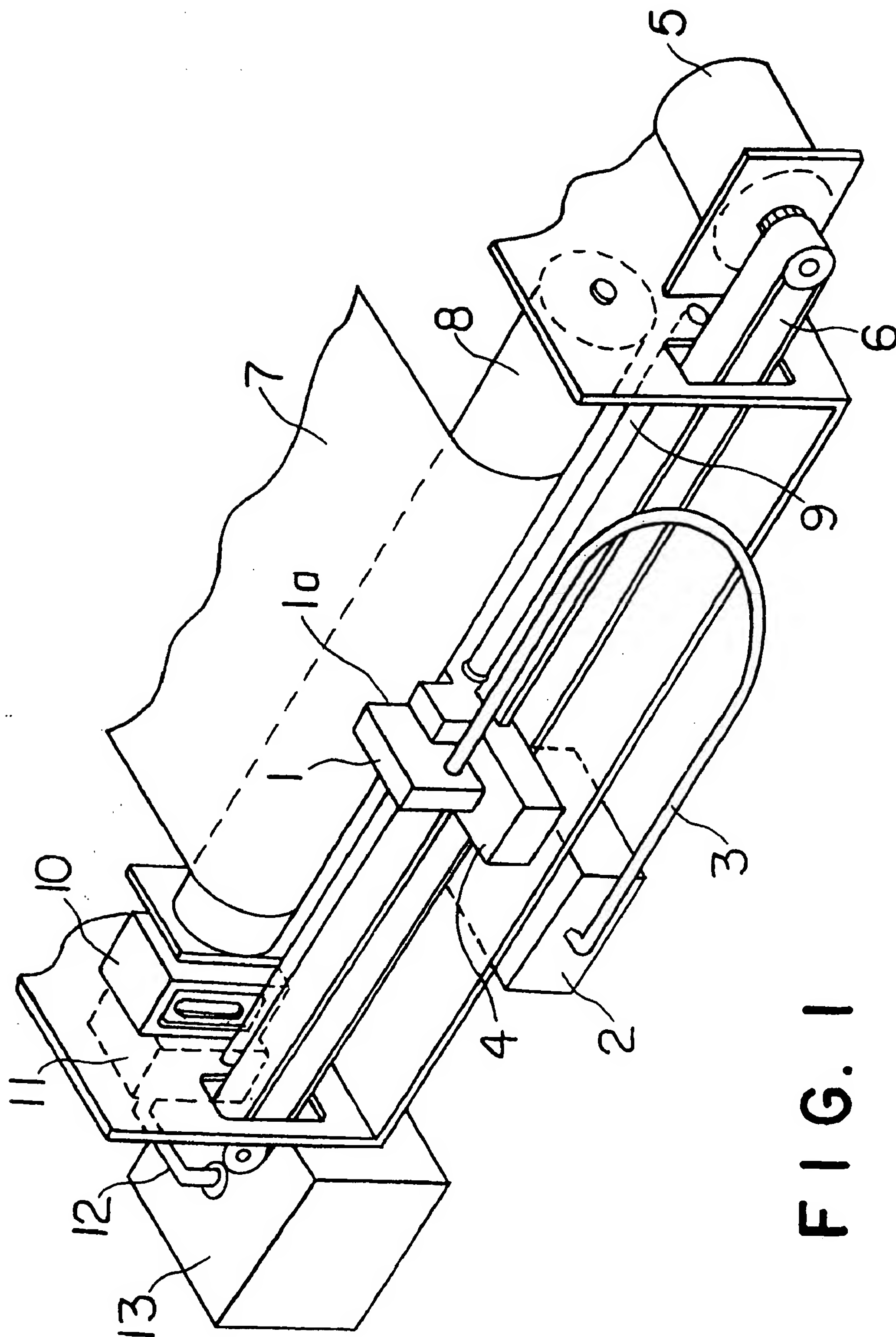


FIG. 1

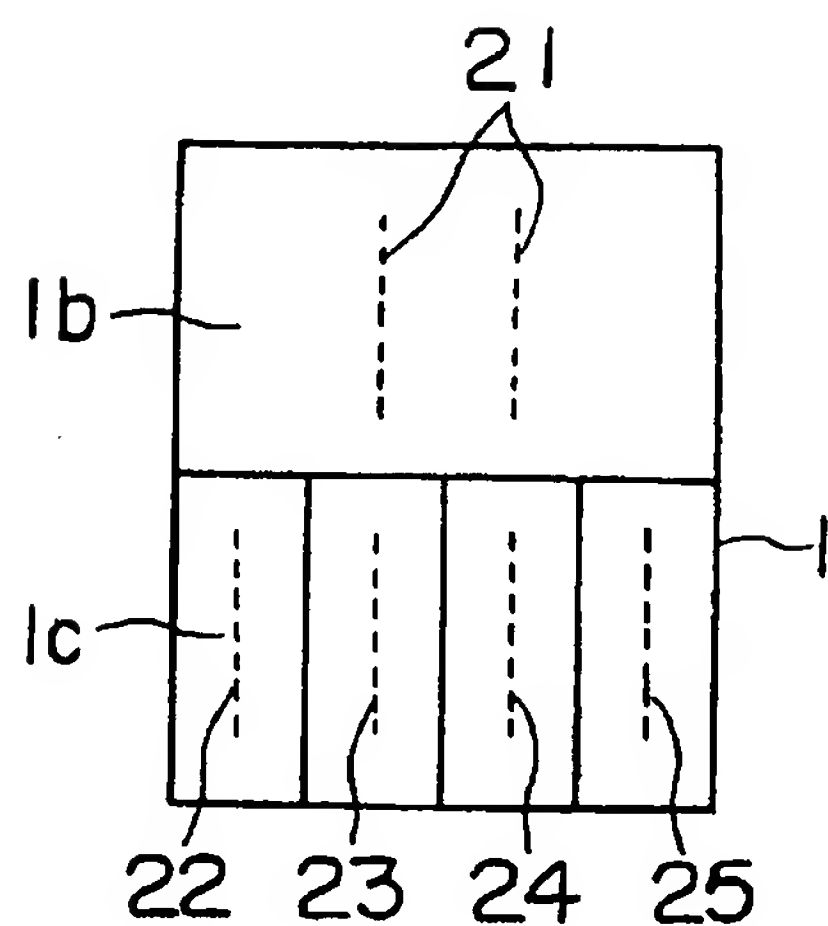


FIG. 2

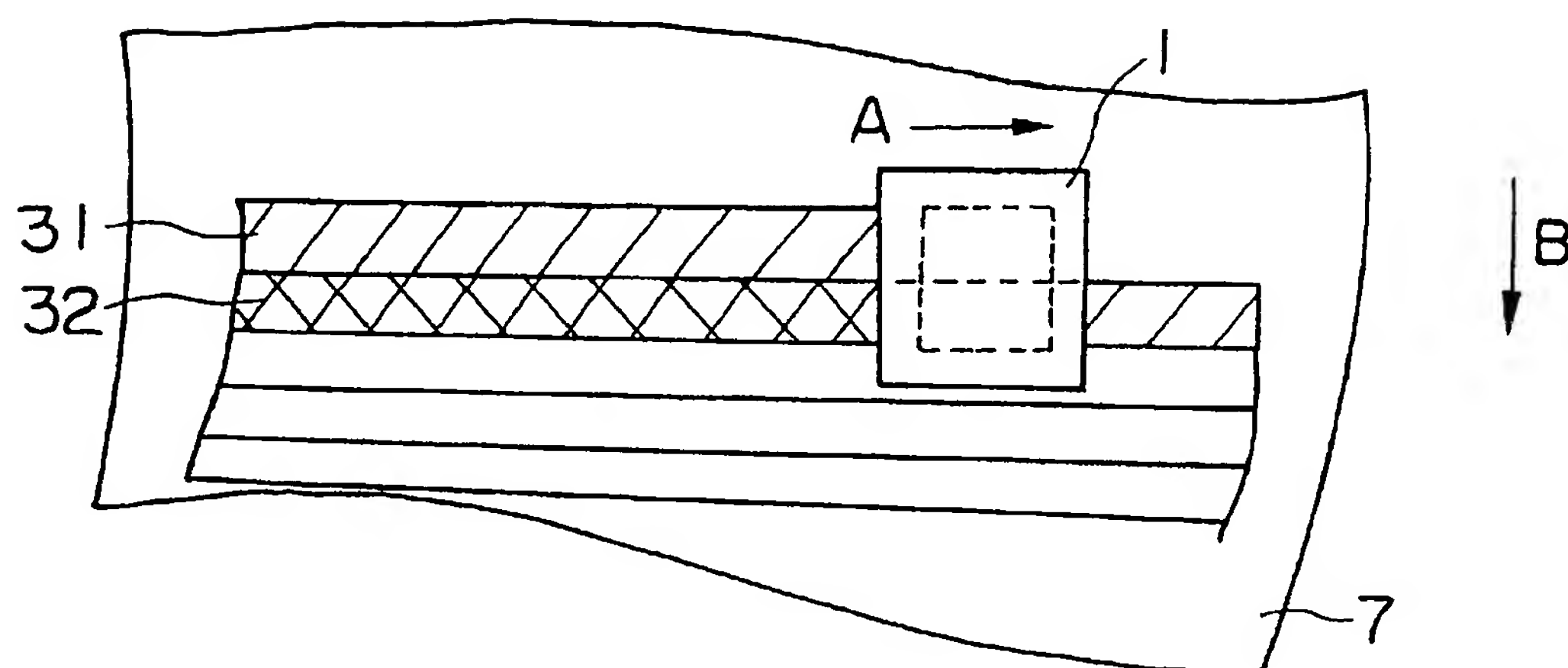


FIG. 3

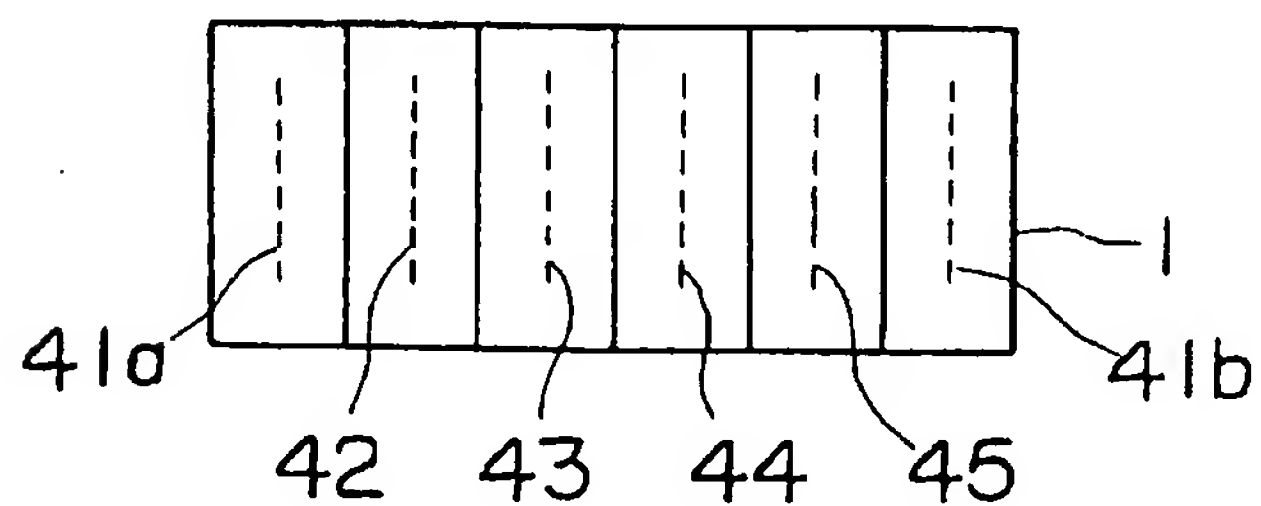


FIG. 4

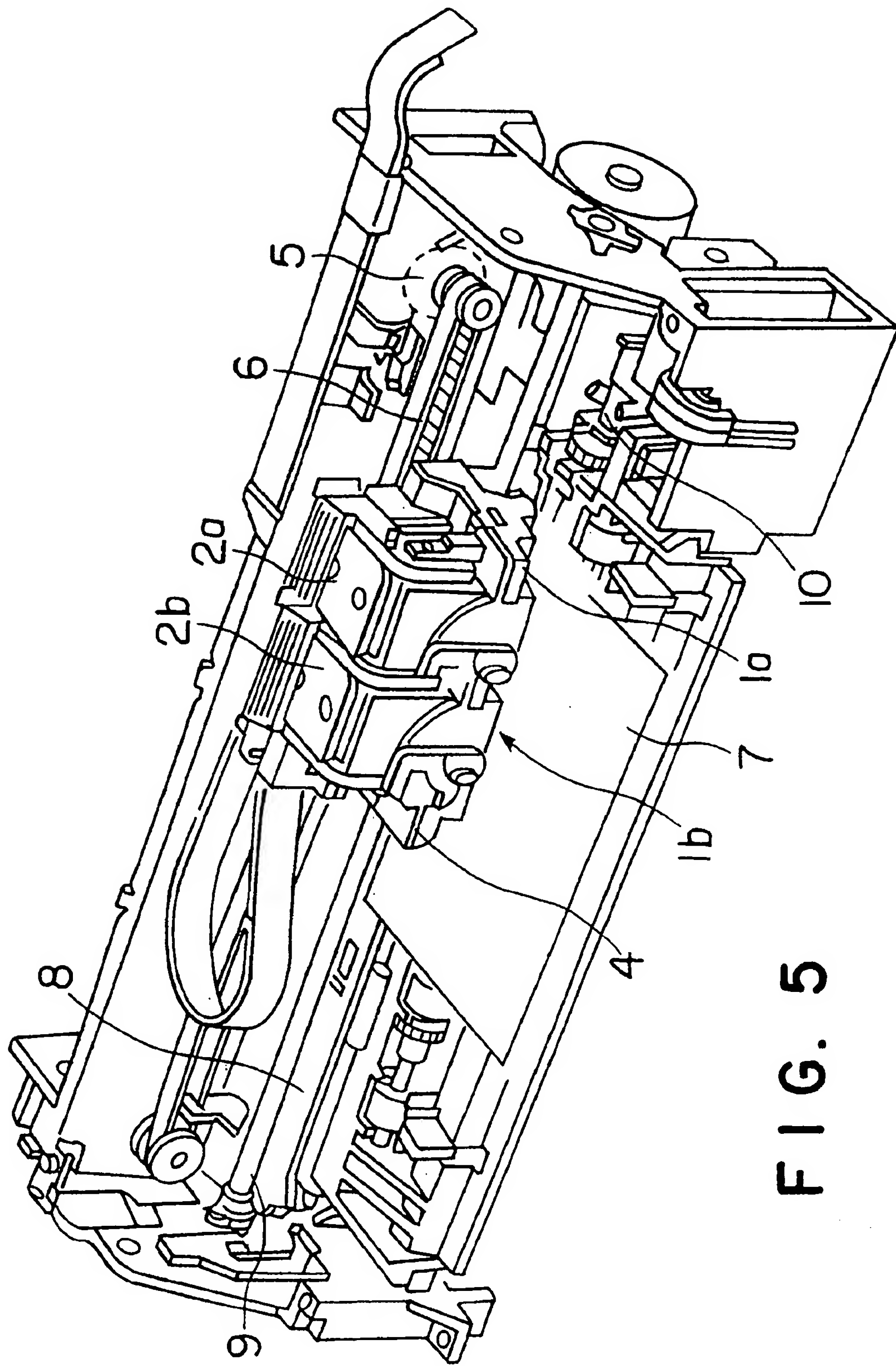


FIG. 5

INK JET RECORDING INK AND RECORDING METHOD

This is a division of application Ser. No. 08/803,339 filed Feb. 20, 1997.

FIELD OF THE INVENTION

The present invention relates to an ink jet recording method. More particularly, the present invention relates to an ink jet recording method wherein both a reaction solution and an ink composition are deposited onto a recording medium.

BACKGROUND ART

An ink jet recording method is a printing method wherein droplets of an ink composition are ejected and deposited onto a recording medium such as paper. This method has a feature that an image having a high resolution and a high quality can be realized at a high speed with a relatively inexpensive apparatus. In general, the ink composition used in the ink jet recording method comprises water as a main component and, added thereto, a colorant and a wetting agent such as glycerin added for prevention of clogging and other purposes.

On the other hand, a new ink jet recording method has been recently proposed. The new method comprises applying a polyvalent metal salt solution onto a recording medium and then applying an ink composition containing a dye having at least one carboxyl group (e.g., Japanese Patent Laid-Open No. 202328/1993). According to this method, polyvalent metal ions combine with the dye to form an insoluble composite which can provide an image having water resistance and a high quality free from color bleeding.

Further, an ink jet recording method has been proposed wherein a color ink containing at least a surfactant or a penetrable solvent and a salt for imparting a penetrating property is used in combination with a black ink which cooperates with the salt to cause thickening or coagulation, thereby providing a high-quality color image having a high image density and free from color bleeding (Japanese Patent Laid-Open No. 106735/1994). More specifically, in this method, two liquids, i.e., a first liquid containing a salt and a second liquid of an ink composition, are printed to provide a good image.

Furthermore, other ink jet recording methods wherein two liquids are printed have been proposed, for example, in Japanese Patent Laid-Open No. 240557/1991 and No. 240558/1991.

In the above ink jet recording method wherein two liquids are printed, a need still exists for the following properties.

At the outset, an improvement in fixability of the colorant is required. In recent years, recycled papers have become used instead of wood free papers. For the recycled papers, the penetration of an ink is in general better than that for the wood free papers. For this reason, a high-quality image is formed on the wood free papers, whereas feathering or color bleeding is often created in the image formed on the recycled papers. Therefore, for recycled paper, the elimination of the feathering or color bleeding has been desired in the art.

Secondly, a reduction in uneven printing is required. The uneven printing refers to a variation in color density in the print derived from localization of a colorant on the paper. Although the uneven printing poses no significant problem in printing of letters of regular size, it is a serious problem in applications where figures, graphs and the like are printed.

Thirdly, broadening the range of usable colorants is required. Most of ink jet recording methods where two liquids are printed utilize a salting-out phenomenon between a metal ion and a carboxyl ion contained in the colorant so that the colorant should have a carboxyl group. Some dyes, however, contain a water-soluble group other than the carboxyl group. For example, some dyes may dissolve with a sulfonic group. A recording method which permits the use of dyes having a group other than a carboxyl group has been desired in the art.

SUMMARY OF THE INVENTION

The present inventors have now found that, in the ink jet recording method wherein two liquids are printed, the use of an ink composition with an oxide colloid added thereto can provide a good print. The present invention has been made based on such finding.

Accordingly, a general object of the present invention is to provide an ink jet recording method involving printing of two liquids which can realize a good image.

A more specific object of the present invention is to provide an ink jet recording method involving printing of two liquids which can realize a good image even on recycled paper.

Another object of the present invention is to provide an ink jet recording method involving printing of two liquids which can realize an image free from uneven printing.

A further object of the present invention is to provide an ink jet recording method involving printing of two liquids which enables a wide range of colorants to be usable.

The above object can be attained, according to the present invention, by an ink jet recording method comprising the step of depositing a reaction solution and an ink composition onto a recording medium to perform printing, wherein the reaction solution contains a polyvalent metal salt and/or polyallylamine and the ink composition comprises at least a colorant, an inorganic oxide colloid, and an aqueous solvent.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows an embodiment of the ink jet recording apparatus according to the present invention, wherein a recording head is provided separately from an ink tank to feed an ink composition and a reaction solution into a recording head through an ink tube;

FIG. 2 is an enlarged view showing the surface of nozzles for a recording head, wherein reference character 1b designates the surface of a nozzle for a reaction solution and 1c the surface of a nozzle for an ink composition;

FIG. 3 is a diagram illustrating ink jet recording using the recording head shown in FIG. 2, wherein numeral 31 designates a region where a reaction solution has been deposited and numeral 32 a printed region where an ink composition has been printed on the deposited reaction solution;

FIG. 4 shows another embodiment of the recording head according to the present invention, wherein all ejection nozzles are arranged in lateral direction;

FIG. 5 shows an embodiment of the ink jet recording apparatus according to the present invention, wherein a recording head is integral with an ink tank; and

DETAILED DESCRIPTION OF THE
INVENTION

Ink jet recording method

The ink jet recording method according to the present invention comprises the step of printing a reaction solution and an ink composition on a recording medium.

The reaction solution and the ink composition may be applied on a recording medium in any sequence. Specifically, any of the following methods may be suitably used: a method wherein a reaction solution is deposited onto a recording medium followed by deposition of an ink composition onto the recording medium with the reaction solution deposited thereon, a method wherein an ink composition is printed followed by deposition of the reaction solution, and a method wherein a reaction solution and an ink composition are mixed together immediately before or immediately after ejection thereof.

According to the ink jet recording method of the present invention, good printing can be realized by bringing a reaction solution into contact with an ink composition. Although the present invention is not intended to be bound by the following hypothesis, the reason why good printing can be achieved by the present invention is believed as follows. Upon contact of the reaction solution with the ink composition, the polyvalent metal ion or the polyallylamine contained in the reaction solution breaks the state of dispersion of a colorant, an inorganic oxide colloid, and other ingredients, resulting in agglomeration of these ingredients. In particular, the polyvalent metal ion or the polyallylamine contained in the reaction solution is reacted with the inorganic oxide colloid contained in the ink composition to form agglomerates which inhibit the penetration of the colorant into the recording medium. Colloidal particles left on the recording medium are deposited onto the recording medium, and the particles are bound to one another to form a film, accelerating the fixation of the colorant onto the recording medium. Thus, an image having high color density and free from feathering and uneven printing could be realized. Further, in a color image, uneven color mixing in boundaries of different colors, that is, color bleeding, can also be advantageously prevented. The above mechanism is hypothetical, and the present invention should not be construed to be limited by this mechanism.

As described above, in the present invention, the inorganic oxide colloid is reacted with the polyvalent metal ion or the polyallylamine contained in the reaction solution to efficiently form agglomerates. Thus, a good printed image can be realized even when the colorant, together with the polyvalent metal ion or the polyallylamine, is less likely to form an agglomerate. This means that the method according to the present invention does not limit the kind of the colorant used and permits a wide variety of colorants to be used, which is a great advantage of the present invention.

The deposition of the reaction solution onto the recording medium may be carried out by any of an embodiment where the reaction solution is selectively deposited on only an area where the ink composition is to be deposited and an embodiment where the reaction solution is deposited on the whole surface of paper. The former embodiment can minimize the consumption of the reaction solution and, hence, is cost-effective. In this embodiment, however, an accuracy is required to some extent with respect to the position where both the reaction solution and the ink composition are deposited. On the other hand, for the latter embodiment, the requirement for the accuracy of the position where the reaction solution and the ink composition are deposited is

relaxed as compared with the former embodiment. In this embodiment, however, since the reaction solution is deposited in a large amount on the whole surface of paper, the paper is likely to cause curling during drying. For the above reason, the selection of the embodiment may be determined by taking a combination of the ink composition with the reaction solution into consideration. In the case of the former embodiment, the deposition of the reaction solution can be performed by ink jet recording.

As described below, the reaction solution may contain a colorant so as to function also as an ink composition.

Ink composition

The ink composition used in the present invention comprises at least a colorant, an inorganic oxide colloid, and an aqueous solvent.

Inorganic oxide colloid

The inorganic oxide colloid which is also called "inorganic oxide sol" used in the present invention refers to a colloidal solution comprising: a dispersion medium composed of water or water and an organic solvent having good compatibility with water; and a dispersoid composed of ultrafine particles of an inorganic oxide. Inorganic oxides usable herein include, but are not limited to, high-molecular weight silicic anhydride (SiO_2) and alumina (Al_2O_3). The particle diameter of the ultrafine particles of the inorganic oxide is generally about 1 to 100 nm, preferably 1 to 20 nm, more preferably 1 to 10 nm. The dispersion medium for the inorganic oxide colloid is generally water or a mixed solvent composed of water and an organic solvent having good compatibility with water, for example, methanol, ethanol, isopropyl alcohol, or n-propanol. The inorganic oxide colloid is prepared by dispersing ultrafine particles of the inorganic oxide into water or the above organic solvent. A dispersion of the ultrafine particles in water is called an "aqueous sol," and a dispersing of the ultrafine particles in an organic solvent is called an "organosol."

As described above, the inorganic oxide colloid used in the present invention should interact with the polyvalent metal salt and/or polyallylamine to form agglomerates.

The inorganic oxide colloid may be a commercially available one, and specific examples thereof include: Snowtex S, Snowtex N, Snowtex C, Snowtex SS, Snowtex XS, Snowtex 20, Snowtex 30, and Snowtex 40, manufactured by Nissan Chemical Industry Ltd., Cataloid SI-350, Cataloid SI-500, Cataloid SI-30, Cataloid S-20L, Cataloid S-20H, Cataloid S-30L, Cataloid S-30H, and Cataloid SI-40, manufactured by E. I. du Pont de Nemours & Co.), which are dispersions of ultraviolet particles of high-molecular weight silicic anhydride in water; Aluminasol 100, Aluminasol 200, and Aluminasol 520, manufactured by Nissan Chemical Industry Ltd., which are dispersions of ultrafine particles of alumina in water; and OSCAL-1432 (isopropyl alcohol sol, manufactured by Catalysts and Chemicals Industries Co., Ltd.) which is a dispersion of ultrafine particles of high-molecular weight silicic anhydride in an organic solvent. Most of the commercially available colloidal solutions of inorganic oxides have pH adjusted to the acidic or alkaline. This is because the pH region where the inorganic oxide colloid exists stably is on the acidic or alkaline side. Therefore, when the addition of a commercially available inorganic oxide colloidal solution to the ink is contemplated, it should be made by taking into consideration the pH region, where the inorganic oxide colloid exists stably, and the pH value of the ink.

The amount of the inorganic oxide colloid added may be suitably determined by taking into consideration the type

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and agglomerate. In general, however, it is preferably about 0.1 to 15% by weight, more preferably about 0.5 to 5.0% by weight, based on the ink composition. A plurality of inorganic oxide colloids may be added.

Colorant

The colorant contained in the ink composition according to the present invention may be any of a dye and a pigment. In the present invention, the following wide variety of colorants may be utilized.

Dyes usable herein include various dyes commonly used in ink jet recording, such as direct dyes, acid dyes, foodstuff dyes, basic dyes, reactive dyes, disperse dyes, vat dyes, soluble vat dyes, and reactive disperse dyes.

Regarding the pigment, inorganic and organic pigments are usable without any particular limitation. Examples of the inorganic pigment include, in addition to titanium oxide and iron oxide, carbon blacks produced by known processes, such as contact, furnace, and thermal processes. Examples of the organic pigment include azo pigments (including azo lake, insoluble azo pigment, condensed azo pigment, and chelate azo pigment), polycyclic pigments (for example, phthalocyanine, perylene, perinone, anthraquinone, quinacridone, dioxazine, thioindigo, isoindolinone, and quinophthalone pigments), dye chelates (for example, basic dye chelates and acid dye chelates), nitro pigments, nitroso pigments, and aniline black.

According to a preferred embodiment of the present invention, the above pigment is preferably added in the form of a pigment dispersion prepared by dispersing the pigment in an aqueous medium with the aid of a dispersant or a surfactant. Preferred dispersants include those commonly used in the preparation of a dispersion of a pigment, for example, polymeric dispersant. In this connection, that the dispersant and the surfactant contained in the dispersion of the pigment function also as the dispersant and the surfactant for the ink composition will be apparent to a person having ordinary skill in the art.

The amount of the pigment added to the ink is preferably about 0.5 to 25% by weight, more preferably about 2 to 15% by weight.

Aqueous Solvent

The aqueous solvent as a main solvent of the ink composition of the present invention comprises basically an water-soluble organic solvent and water. The water-soluble organic solvent is preferably a low-boiling organic solvent, and preferred examples thereof include methanol, ethanol, n-propyl alcohol, iso-propyl alcohol, n-butanol, sec-butanol, tert-butanol, iso-butanol, and n-pentanol. Monohydric alcohols are particularly preferred. The low-boiling organic solvent has the effect of shortening the time taken for drying the ink.

Further, according to a preferred embodiment of the present invention, the aqueous solvent further comprises a wetting agent comprising a high-boiling organic solvent. Preferred examples of high-boiling organic solvents usable herein include polyhydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, polypropylene glycol, propylene glycol, butylene glycol, 1,2,6-hexanetriol, thioglycol, hexylene glycol, glycerin, trimethylethane, and trimethylolpropane; alkyl ethers of polyhydric alcohols, such as ethylene glycol monomethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, and triethylene glycol monobutyl ether; urea; 2-pyrrolidone;

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N-methyl-2-pyrrolidone; 1,3-dimethyl-2-imidazolidinone; and triethanolamine.

The amount of the wetting agent added is preferably in the range of from 0.5 to 40% by weight, more preferably in the range of from 2 to 20% by weight, based on the ink. The amount of the low-boiling organic solvent added is preferably 0.5 to 10% by weight, more preferably in the range of from 1.5 to 6% by weight, based on the ink.

The ink composition used in the present invention may contain a surfactant. Preferred examples thereof include surfactants such as anionic surfactants, nonionic surfactants, and amphoteric surfactants, alcohol such as methanol, and iso-propyl alcohol, and polyalcohol lower alkyl ether such as ethylene glycol mono-methyl ether, diethylene glycol mono-methyl ether, diethylene glycol mono-butyl ether, triethylene glycol mono-butyl ether, propylene glycol mono-methyl ether, and dipropylene glycol mono-methyl ether.

Further, if necessary, pH adjustors, preservatives, antimolds and the like may be added. Examples of pH adjustors include KOH, NaOH, triethanolamine.

Saccharide

The ink composition used in the present invention may further comprise a saccharide. The addition of the saccharide can further improve the color density, minimizing feathering and uneven printing. Further, in the case of a color image, color bleeding can be prevented on a high level. Specific examples of saccharides usable herein include monosaccharides, disaccharides, oligosaccharides (including trisaccharides and tetrasaccharides), and other polysaccharides, preferably glucose, mannose, fructose, ribose, xylose, arabinose, galactose, aldonic acid, glucitol, sorbitol, maltose, cellobiose, lactose, sucrose, trehalose, and maltotriose. The term "polysaccharide" used herein means saccharides in the broad sense as including substances which exist widely in the world of nature, such as alginic acid, α -cyclodextrin, and cellulose. Derivatives of these saccharides usable herein include reducing sugars of the above saccharides (for example, sugar alcohols represented by the general formula $\text{HOCH}_2(\text{CHOH})_n\text{CH}_2\text{OH}$, wherein n is an integer of 2 to 5), oxidizing sugars (for example, aldonic acid or uronic acid), amino acids, and thiosugars. Among them, sugar alcohols are particularly preferred, and specific examples thereof include maltitol and sorbitol.

The content of the saccharide is suitably 0.1 to 40% by weight, preferably 0.5 to 30% by weight, based on the ink composition.

Epoxy-containing compound and epoxy curing agent

According to a preferred embodiment of the present invention, the ink composition according to the present invention contains an epoxy-containing compound. The term "epoxy-containing compound" used herein means a compound which has at least two epoxy groups in its molecular structure and causes a crosslinking reaction, in which an epoxy group is involved, resulting in resinification (i.e., increased molecular weight). The addition of the epoxy-containing compound permits good scratch resistance and water resistance to be imparted to the printed image.

Epoxy-containing compounds usable in the present invention include compounds containing an epoxy group and, in addition, a functional group reactive with an epoxy group and compounds containing an epoxy group but not containing a functional group reactive with an epoxy group.

The term "functional group reactive with an epoxy group" used herein means a functional group which is reacted with an epoxy group to cause crosslinking, and examples of such

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functional groups include hydroxyl, carboxyl, and sulfonic groups. In the present invention, the use of the epoxy-containing compound having a functional group reactive with an epoxy group can eliminate; the need to add an epoxy curing agent, described below, to the reaction solution. On the other hand, the addition of an epoxy curing agent to the reaction solution in combination with the use of the epoxy-containing compound having a functional group reactive with an epoxy group results in further improved fixation rate of the print. Any one of these advantages may be selected depending upon situation.

The mechanism through which the addition of an epoxy-containing compound to the ink composition according to the present invention can offer a good print is believed as follows. However, the following mechanism is hypothetical, and the present invention should not be construed to be limited by this mechanism.

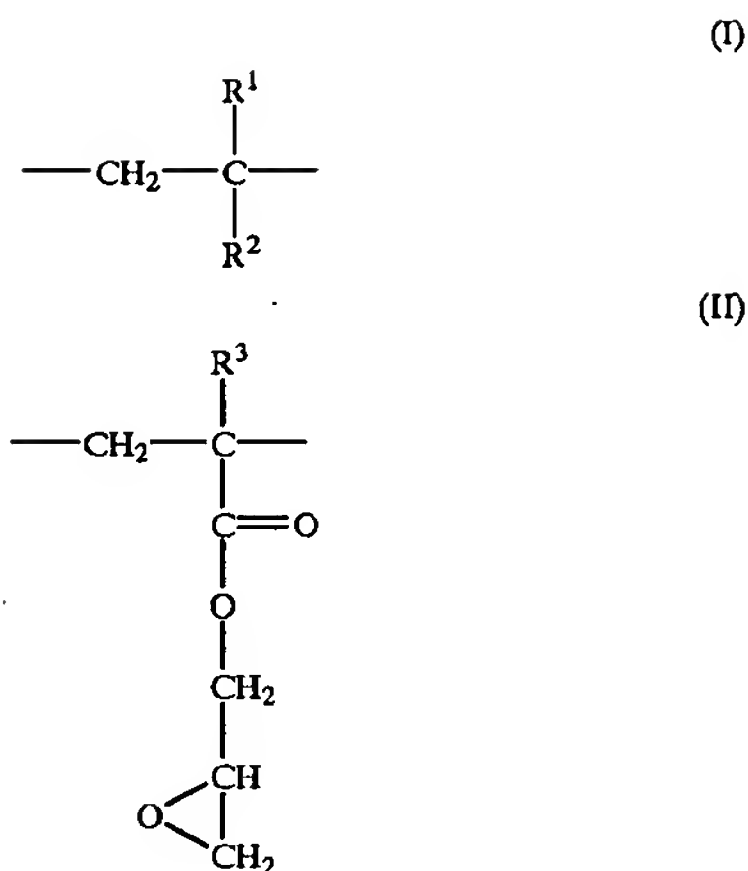
In the method according to the present invention, a reaction solution is and an ink composition are deposited onto a recording medium. As described above, upon the deposition of the ink composition onto the recording medium, interaction between a polyvalent metal ion derived from a polyvalent metal salt or a polyallylamine in the reaction solution and an inorganic oxide colloid in the ink composition results in agglomeration. When the reaction solution contains an epoxy-curing agent, crosslinking of the epoxy group in the epoxy-containing compound occurs resulting in resinification. On the other hand, it is considered that when the compound having a functional group reactive with an epoxy group is used as the epoxy-containing compound, the resinification proceeds through the following mechanism despite the absence of an epoxy-curing agent. When the distance between the epoxy-containing compounds is decreased by the agglomeration due to the interaction between the polyvalent meal salt or the polyallylamine in the reaction solution and the inorganic oxide colloid in the ink composition, a reaction of the epoxy group with the functional group reactive with the epoxy group would occur among adjacent epoxy-containing compounds. This reaction is considered to cause crosslinking among the epoxy-containing compounds, resulting in resinification. The resinification permits a printed image to be strongly fixed to the recording medium and, in addition, results in the formation of a resin film on the surface of the printed image. Such a print is considered to have good scratch resistance, waterfastness, and lightfastness.

In this context, it should be noted that a reaction between the epoxy-containing compounds each having a functional group reactive with an epoxy group in the ink composition is apparently unfavorable. Therefore, preferably, use of such epoxy-containing compounds is avoided.

Epoxy-containing compounds which may be preferably used in the present invention include epoxy-containing resin emulsions and water-soluble epoxy compounds.

According to a preferred embodiment of the present invention, epoxy-containing resin emulsions include an epoxy-containing acrylic resin emulsion comprising: a continuous phase of water; and a dispersed phase comprising a copolymer comprised of recurring units represented by the following formulae (I) and (II):

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wherein

R¹ and R³ each independently represent H or CH₃;

R² represents a group containing in its structure at least one group selected from alkyl (with C₁₋₂₁ alkyl being preferred), hydroxyl, carboxyl and sulfonic groups. This resin is not limited by the form of copolymers, and, for example, a block copolymer and a random copolymer are possible.

For the above copolymers, the terminal thereof has no essential influence on the properties because the polymer has a high molecular weight. In general, a fragment of a polymerization initiator constitutes the terminal, and examples of such fragments include fragments of ammonium persulfate and potassium persulfate, such as —OSO₃H.

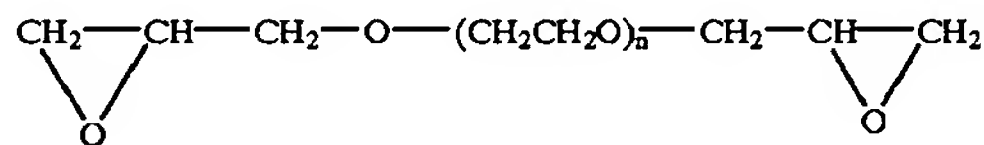
Examples of preferred R² include —OH, —COOH, or —COO—R (wherein R represents a straight or branched alkyl group, preferably a C₁₋₁₂ alkyl group with at least one hydrogen atom on the alkyl group being optionally substituted by a hydroxyl, phosphono, or sulfonic group), and an aryl group substituted by a sulfonic group such as for example, a phenyl or tolyl group. Specific examples of the group represented by R² include —OH, —COOH, —COOCH₂CH₂OH, —COOCH₂CH(CH₃)OH, —COOCH₂CH₂PO(OH)₂, —C₆H₅SO₃H, —COOCH₂CH₂SO₃H, —COOCH₃, —COOC₂H₅, —COOC₄H₉, —COOC₆H₁₃, —COO(CH₂)₁₁CH₃, and —COOCH₂CH(CH₃)CH₂C(CH₃)₃. In this context, a hydroxyl, carboxyl, or sulfonic group which may be contained in R² is a functional group reactive with an epoxy group. Therefore, when R² contains an alkyl group alone and when R² contains a hydroxyl, carboxyl, or sulfonic group but does not substantially react with an epoxy group, the resin emulsion does not have any functional group reactive with an epoxy group. On the other hand, when R² contains a hydroxyl, carboxyl, or sulfonic group in addition to an alkyl group, the resin emulsion has a functional group reactive with an epoxy group.

Commercially available resin emulsions may be used, and examples thereof include Almatex Z116 (manufactured by Mitsui Toatsu Chemicals, Inc.), NEW COAT S2170 and NEW COAT S-1080 (manufactured by Shin-Nakamura Chemical Co., Ltd.), VANATEX #952 and VANATEX HG-9 (manufactured by Shin-Nakamura Chemical Co., Ltd.), and Piestex B-3 (manufactured by Shin-Nakamura Chemical Co., Ltd.).

The water-soluble epoxy compound comprises at least two, per molecule, epoxy groups reactive with an epoxy-

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curing agent described below, and typical examples thereof include water-soluble diepoxides. Water-soluble epoxy compounds which may be preferably used in the present invention include compounds represented by the following formula.



wherein n is a natural number of 4 to 9.

Examples of preferred water-soluble epoxy compounds include polyethylene glycol glycidyl ether. Commercially available water-soluble epoxy compounds usable herein include Epolight 400E (polyethylene glycol #400 glycidyl ether, manufactured by Kyoisha Chemical Co., Ltd.), Epolight 200E (polyethylene glycol #200 glycidyl ether, manufactured by Kyoisha Chemical Co., Ltd.), Epolight 80MF (glycerin diglycidyl ether, manufactured by Kyoisha Chemical Co., Ltd.), Epiall G-100 (glycerin diglycidyl ether, manufactured by Nippon Oils & Fats Co., Ltd.), and Denacol (manufactured by Nagase Chemicals Ltd.).

Examples of epoxy-containing compounds, having a functional group reactive with an epoxy group, which may be preferably used in the present invention include those, among the above epoxy-containing resin emulsions, wherein at least part of R² contains a functional group reactive with an epoxy group, that is, a functional group selected from hydroxyl, carboxyl, and sulfonic groups. It is also possible to use an epoxy-containing compound wherein R² partly contains an alkyl group, preferably a C₁₋₂₁ alkyl, and does not contain any functional group reactive with an epoxy group. Commercially available epoxy-containing compounds of the above type include Almatex Z116 (manufactured by Mitsui Toatsu Chemicals, Inc.).

The content of the epoxy-containing compound in the ink composition according to the present invention is preferably about 1 to 10% by weight, more preferably 1 to 5% by weight, based on the ink composition.

The ink composition used in the present invention may contain a resin emulsion as described below. When the above epoxy-containing compound is an epoxy-containing resin emulsion, it serves also as the resin emulsion. Therefore, use of an additional resin emulsion is unnecessary. However, according to a preferred embodiment of the present invention, the resin emulsion is added in combination with the epoxy-containing resin emulsion.

In the present invention, preferably, an epoxy-curing agent may be incorporated into the reaction solution. This epoxy-curing agent refers to an agent which, together with the epoxy-containing compound contained in the ink composition, accelerates resinification (an increase in molecular weight) of the epoxy-containing compound by crosslinking. According to the present invention, any epoxy-curing agent may be utilized without any limitation so far as it can offer a printed image having good scratch resistance and waterfastness in the ink jet recording method described below.

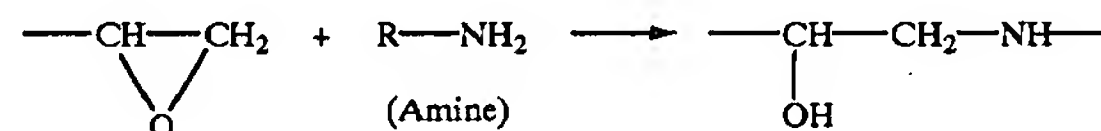
Epoxy-curing agents which may be preferably used in the present invention are typically soluble in water. Examples thereof include amine compounds, for example, ethylenediamine, diethylaminopropylamine, N-aminoethylpiperazine, trimethylhexamethylenediamine, modified aliphatic amines, water-soluble polyamines, water-soluble cold curing catalysts other than amines, for example, aromatic sulfonic acid, such as p-phenolsulfonic acid, and curing agents for epoxy emulsions. It is also possible to

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utilize commercially available curing agents, and examples thereof include Almatex H700 (manufactured by Mitsui Toatsu Chemicals, Inc.) and EPOKY-H (manufactured by Mitsui Toatsu Chemicals, Inc.).

The concentration of the epoxy-curing agent in the reaction solution is preferably about 0.1 to 40% by weight, more preferably about 1 to 20% by weight.

According to the present invention, upon printing of an ink composition on a recording medium with a reaction solution deposited thereon, an epoxy-curing agent contained in the reaction solution is reacted with an epoxy-containing compound contained in the ink composition, to permit crosslinking of the epoxy-containing compound to proceed. This reaction may be expressed, for example, by the following formula:



This accelerates the resinification of the epoxy-containing compound (a further increase in molecular weight of the resin emulsion). The above resinification in a printed image formed on a recording medium permits the printed image to be strongly adhered to the recording medium and, in addition, results in the formation of a resin film on the surface of the printed image. Thus, the print has good scratch resistance, waterfastness, and lightfastness.

Resin emulsion

According to a preferred embodiment of the present invention, the ink composition used in the present invention contains a resin emulsion. A preferred resin emulsion comprises a continuous phase of water and a dispersed phase comprising a resin not containing an epoxy group. As described above, when the epoxy-containing compound is an epoxy-containing resin emulsion, the addition of the resin emulsion is not essential. Resins usable herein include acrylic resin, vinyl acetate resin, styrene-butadiene resin, vinyl chloride resin, (meth)acrylate-styrene resin, butadiene resin, and styrene resin.

Further, commercially available resin emulsions may also be used, and examples thereof include Microgel E-1002 and E-5002 (styrene/acrylic resin emulsion, manufactured by Nippon Paint Co., Ltd.), Voncoat 4001 (acrylic resin emulsion, manufactured by Dainippon Ink and Chemicals, Inc.), Voncoat 5454 (styrene/acrylic resin emulsion, manufactured by Dainippon Ink and Chemicals, Inc.), SAE-1014 (styrene/acrylic resin emulsion, manufactured by Nippon Zeon Co., Ltd.), and Saivinol SK-200 (acrylic resin emulsion, manufactured by Sainen Chemical Industry Co., Ltd.).

According to a preferred embodiment of the present invention, the resin is a polymer having a combination of a hydrophilic segment with a hydrophobic segment. The particle diameter of the resin component is not particularly limited so far as the resin component forms an emulsion. It, however, is preferably not more than about 150 nm, more preferably about 5 to 100 nm.

The resin emulsion may be prepared by subjecting a monomer(s) for forming a contemplated resin to dispersion polymerization in water optionally in the presence of a surfactant. For example, an emulsion of an acrylic resin or a styrene/acrylic resin may be prepared by subjecting an ester of (meth)acrylic acid or alternatively an ester of (meth)acrylic acid in combination with styrene to dispersion polymerization in water optionally in the presence of a surfactant. In general, the ratio of the resin component to the

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surfactant is preferably about 10:1 to 5:1. When the amount of the surfactant used falls within the above range, it is possible to provide an ink which has good water resistance in the form of an image and good penetrability. The surfactant is not particularly limited. Preferred examples thereof include anionic surfactants (for example, sodium dodecylbenzenesulfonate, sodium laurate and an ammonium salt of a polyoxyethylene alkyl ether sulfate); nonionic surfactants having 10 or more of HLB value (for example, a polyoxyethylene alkyl ether, a polyoxyethylene alkyl ester, a polyoxyethylene sorbitan fatty acid ester, a polyoxyethylene alkylamine, and a polyoxyethylene alkylamide). They may be used alone or as a mixture of two or more. Further, it is also possible to use acetylene glycol (OLFINE Y and Surfynol 82, 104, 440, 465, and 485 (all the above products being manufactured by Air Products and Chemicals Inc.).

The ratio of the resin as the component constituting the dispersed phase to water is suitably 60 to 400 parts by weight based on 100 parts by weight of the resin with 100 to 200 parts by weight, based on 100 parts by weight of the resin, of water being preferred.

The ratio of the resin as the component constituting the dispersed phase to water is suitably 60 to 400 parts by weight based on 100 parts by weight of the resin with 100 to 200 parts by weight, based on 100 parts by weight of the resin, of water being preferred.

In the ink used in the present invention, the amount of the resin emulsion incorporated therein is preferably such that the amount of the resin component is in the range of from 0.1 to 40% by weight, more preferably in the range of from 1 to 25% by weight.

For both the resin emulsion containing an epoxy group and the resin emulsion not containing an epoxy group, it is considered that interaction between these resin emulsions and the polyvalent metal ion inhibits the penetration of the colorant component and accelerates the fixation of the colorant component to the recording medium.

Reaction solution

The reaction solution used in the present invention basically comprises a polyvalent metal salt and/or polyallylamine and water. When the ink composition contains an epoxy-containing compound, the reaction solution preferably further comprises the above-described epoxy-curing agent.

According to the present invention, the polyvalent metal salt contained in the reaction solution may comprise a divalent or higher polyvalent metal ion and an ion bonded to the polyvalent metal, preferably a nitrate ion or a carboxylate ion and is soluble in water.

Furthermore, preferably, the carboxylate ions are derived from a saturated aliphatic monocarboxylic acid having 1 to 6 carbon atoms or a carbocyclic monocarboxylic acid having 7 to 11 carbon atoms. Preferred examples of the saturated aliphatic monocarboxylic acid having 1 to 6 carbon atoms include formic acid, acetic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, isovaleric acid, pivalic acid, and hexanoic acid. Among them, formic acid and acetic acid are particularly preferred.

A hydrogen atom(s) on the saturated aliphatic hydrocarbon residue in the monocarboxylic acid may be substituted by a hydroxyl group. Preferred examples of such carboxylic acids include lactic acid.

Preferred examples of the carbocyclic monocarboxylic acid having 6 to 10 carbon atoms include benzoic acid and naphthoic acid with benzoic acid being more preferred.

Specific examples of polyvalent metallic ions include divalent metallic ions, such as Ca^{2+} , Cu^{2+} , Ni^{2+} , Mg^{2+} , Zn^{2+} ,

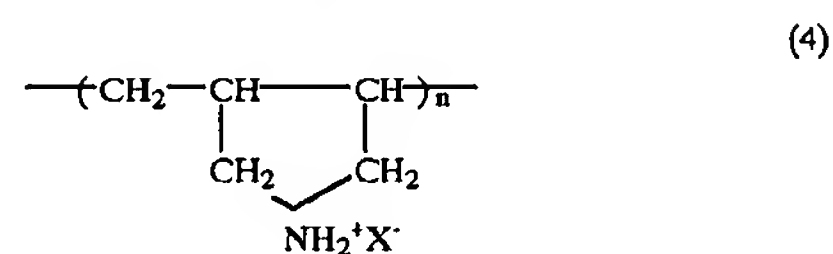
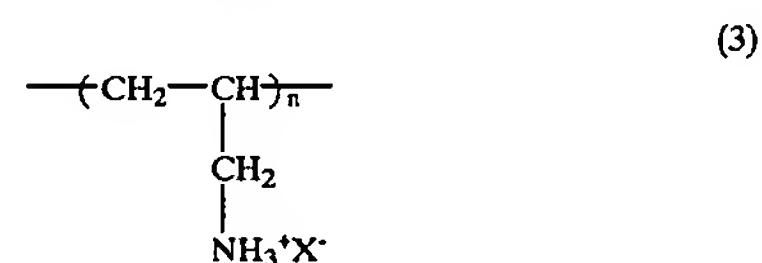
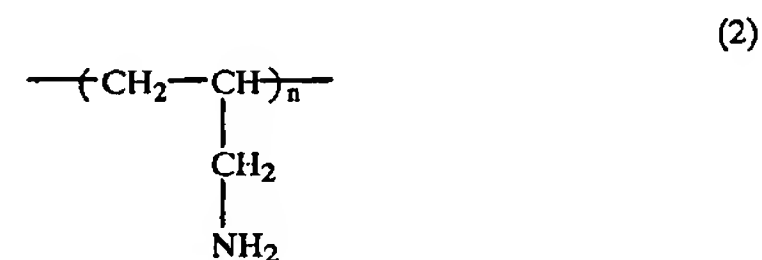
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and Ba^{2+} , trivalent metallic ions, such as Al^{3+} , Fe^{3+} , and Cr^{3+} . Anions include Cl^- , NO_3^- , I^- , Br^- , ClO_3^- , and CH_3COO^- .

In particular, a metal salt constituted by Ca^{2+} or Mg^{2+} provides favorable results in terms of pH of the reaction solution and the quality of prints.

The concentration of the polyvalent metal salt in the reaction solution may be suitably determined so as to attain the effect of providing a good print quality and preventing clogging. It, however, is preferably about 0.1 to 40% by weight, more preferably about 5 to 25% by weight.

The polyallylamines usable in the reaction solution are cationic polymers which are soluble in water and can be positively charged in water. Such polymers include, for example, those represented by the following formulae (2), (3) and (4):



wherein X^- represents at least one member selected from chloride, bromide, iodide, nitrate, phosphate, sulfate, acetate and other ions.

In addition, a copolymer of an allylamine with a diallylamine and a copolymer of diallylmethylammonium chloride with sulfur dioxide may also be used.

The content of the polyallylamine and the polyallylamine derivative is preferably 0.5 to 10% by weight based on the reaction solution.

According to a preferred embodiment of the present invention, the reaction solution may comprise a wetting agent comprising a high-boiling organic solvent. The high-boiling organic solvent serves to prevent the reaction solution from being concentrated due to evaporation, thus preventing clogging of a recording head. Preferred examples of high-boiling organic solvents, some of which are those described above in connection with the ink composition.

Although the amount of the high-boiling organic solvent added is not particularly limited, it is preferably about 0.5 to 40% by weight, more preferably about 2 to 20% by weight.

According to a preferred embodiment of the present invention, triethylene glycol mono-butyl ether and glycerine are preferred. The amount of triethylene glycol mono-butyl ether and glycerine added in combination as the high-boiling organic solvent is preferably in the range of from 10 to 20% by weight, more preferably in the range of from 1 to 15% by weight.

Further, a colorant, e.g., yellow, magenta, or cyan colorant, may be added to the reaction solution so that the colored reaction solution can serve also as the ink composition described below in the paragraph of "Ink composition."

Further, if necessary, pH adjustors, preservatives, antimolds and the like may be added. Examples of pH adjustors

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include KOH, NaOH, triethanolamine. The amount of triethanolamine added is preferably in the range of 0 to 2.0 by weight.

Ink jet recording apparatus

An ink jet recording apparatus for practicing the ink jet recording method according to the present invention will now be described with reference to the accompanying drawings.

FIG. 1 is a diagram showing an embodiment of an ink jet recording apparatus. In this embodiment, an ink composition and a reaction solution are accommodated in a tank and fed into a recording head through an ink tube. Specifically, a recording head 1 is communicated with an ink tank 2 through an ink tube 3. The interior of the ink tank 2 is partitioned, and a chamber for an ink composition, optionally a plurality of chambers respectively for a plurality of color ink compositions, and a chamber for a reaction solution are provided.

The recording head 1 is carried by a carriage 4 and moved along a guide 9 by a timing belt 6 driven by a motor 5. On the other hand, paper 7 as a recording medium is placed by a platen 8 at a position facing the recording head 1. In this embodiment, a cap 10 is provided. A suction pump 11 is connected to the cap 10 in order to conduct the so-called "cleaning operation." The ink composition sucked by the pump 11 is resorvoired in a waste ink tank 13 through a tube 12.

FIG. 2 is an enlarged view showing the surface of nozzles for the recording head 1. In the drawing, the surface of a nozzle for a reaction solution is indicated by 1b, and a nozzle 21 for ejecting the reaction solution is provided in the longitudinal direction. On the other hand, the surface of nozzles for the ink composition is indicated by 1c, and a yellow ink composition, a magenta ink composition, a cyan ink composition, and a black ink composition are ejected respectively through nozzles 22, 23, 24 and 25.

Further, an ink jet recording method using the recording head shown in FIG. 2 will be described with reference to FIG. 3. The recording head 1 is moved in the direction indicated by an arrow A, during which time the reaction solution is ejected through the nozzle 21 to form a reaction solution-deposited region 31 in a band form on the recording medium 7. Subsequently, the recording medium 7 is transferred by a predetermined extent in the direction indicated by an arrow B, during which time the recording head 1 is moved the direction opposite to that indicated by the arrow A and returned to the left end of the recording medium 7, and the recording head conduct printing using the ink composition on the reaction solution-deposited region 31, thereby forming a print region 32.

Further, as shown in FIG. 4, in the recording head 1, it is also possible to arrange all nozzles in the lateral direction to construct a nozzle assembly. In the drawing, ejection nozzles for a reaction solution are denoted by 41a and 41b, and a yellow ink composition, a magenta ink composition, a cyan ink composition, and a black ink composition are ejected respectively through nozzles 42, 43, 44 and 45. In the recording head according to this embodiment, the recording head 1, when reciprocated on the carriage, can conduct printing in both directions. Therefore, in this case, printing at a higher speed is expected as compared with the case where the recording head shown in FIG. 2 is used.

Further, when the reaction solution and the ink composition are preferably adjusted so as to fall within the surface tension ranges described above, a high-quality print can be more stably provided regardless of the order of deposition of the reaction solution and the ink composition. In this case,

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even the provision of a single ejection nozzle suffices for satisfactory results. For example, in the drawing, the nozzle 41b may be omitted. This can contribute to a further reduction in size of the head and a further increase in printing speed.

In the ink jet recording apparatus, the supplement of the ink composition may be carried out by replacing an ink tank in a cartridge form. The ink tank may be integral with the recording head. A preferred embodiment of an ink jet recording apparatus using such an ink tank is shown in FIG. 5. In the drawing, the same members as used in the apparatus shown in FIG. 1 have the same reference numerals. In the embodiment shown in FIG. 5, recording heads 1a and 1b are integral respectively with ink tanks 2a and 2b. An ink composition and a reaction solution are ejected respectively through the recording heads 1a and 1b. Basically, printing may be conducted in the same manner as described above in connection with the apparatus shown in FIG. 1. Further, in this embodiment, the recording head 1a is moved together with the ink tank 2a on a carriage 4, while the recording head 1b is moved together with the ink tank 2b on the carriage 4.

EXAMPLES

The present invention will now be described in more detail with reference to the following examples, though it is not limited to these examples only.

Preparation of ink compositions

The following ink compositions were prepared.

Black ink A1	
Carbon black MA7 (manufactured by Mitsubishi Kasei Corp.)	5% by weight
Styrene/acrylic acid copolymer (dispersant)	1% by weight
Snowtex S (colloidal silica, SiO ₂ content 30%, manufactured by Nissan Chemical Industry Ltd.)	10% by weight
Sucrose	0.7% by weight
Maltitol	6.3% by weight
Glycerin	10% by weight
2-Pyrrolidone	2% by weight
Ethanol	4% by weight
Pure water	Balance

Carbon black and the dispersant were mixed together and dispersed by means of a sand mill (manufactured by Yasukawa Seisakusho) with glass beads (diameter: 1.7 mm, amount: 1.5 times, by weight, the amount of the mixture) for 2 hr. Thereafter, the glass beads were removed, and the remaining additives were added, and the mixture was stirred at room temperature for 20 min and then filtered through a 5-μm membrane filter to prepare an ink for ink jet recording.

Black ink A2	
Carbon black Raven 1080 (manufactured by Columbian Carbon)	5% by weight
Styrene/acrylic acid copolymer (dispersant)	1% by weight
Snowtex C (colloidal silica, (SiO ₂ content 20%), manufactured by Nissan Chemical Industry Ltd.)	0.5% by weight
Sucrose	0.7% by weight

-continued

Maltitol	6.3% by weight	5	
Glycerin	10% by weight		
2-Pyrrolidone	2% by weight		
Ethanol	4% by weight		
Pure Water	Balance		
<u>Black ink A3</u>			
Carbon black Raven 1080	5% by weight	10	
Styrene/acrylic acid copolymer (dispersant)	1% by weight		
Snowtex S	5% by weight		
Voncoat 4001	5% by weight		
(acrylic resin emulsion, resin content 50%, MFT 5° C., manufactured by Dainippon Ink and Chemicals, Inc.)			
Sucrose	0.7% by weight	15	
Maltitol	6.3% by weight		
Glycerin	10% by weight		
2-Pyrrolidone	2% by weight		
Ethanol	4% by weight		
Pure water	Balance	20	
<u>Black ink A4</u>			
C.I. Food Black	2% by weight		25
Snowtex C	10% by weight		
2-Pyrrolidone	5% by weight		
Pure water	Balance		
<u>Black ink A5</u>			
C.I. Food Black	2% by weight	30	
Aluminasol-200	5% by weight		
(Al ₂ O ₃ content 10%, manufactured by Nissan Chemical Industry Ltd.)			
2-Pyrrolidone	5% by weight		
Pure water	Balance		
<u>Black ink A6</u>			
C.I. Food Black	2% by weight	35	
2-Pyrrolidone	5% by weight		
Pure water	Balance		
<u>Black ink A7</u>			
Carbon black Raven 1080	5% by weight		40
Styrene/acrylic acid copolymer (dispersant)	1% by weight		
Sucrose	0.7% by weight		
Maltitol	6.3% by weight		
Glycerin	10% by weight		
2-Pyrrolidone	2% by weight	45	
Ethanol	4% by weight		
Pure water	Balance		

The following colorants were added to the following liquid media to prepare cyan, magenta, and yellow ink compositions as a color ink set.

<u>Color ink set A1</u>		
<u>Dye</u>		55
Cyan ink	3% by weight	60
C.I. Direct Blue 86		
Magenta ink	3% by weight	
C.I. Direct Red 9		
Yellow ink	3% by weight	
C.I. Acid Yellow 23		65
Liquid medium		
Snowtex C	5% by weight	
Diethylene glycol	10% by weight	
Surfynol 82	3% by weight	
Surfynol TG	0.5% by weight	
Pure water	Balance	

-continued

<u>Color ink set A2</u>		
<u>Pigment</u>		
Cyan ink	2% by weight	25
Pigment KETBLUEEX-1 (manufactured by Dainippon Ink and Chemicals, Inc.)		
Magenta ink	2% by weight	
Pigment KETRED 309 (manufactured by Dainippon Ink and Chemicals, Inc.)		
Yellow ink	2% by weight	
Pigment KETYELLOWQ 403 (manufactured by Dainippon Ink and Chemicals, Inc.)		30
Liquid medium		
Styrene/acrylic acid copolymer (dispersant)	0.4% by weight	
Colloidal silica S	3% by weight	
Sucrose	0.7% by weight	
Maltitol	6.3% by weight	35
Glycerin	10% by weight	
2-Pyrrolidone	2% by weight	
Ethanol	4% by weight	
Pure water	Balance	

The following ingredients were mixed together to prepare reaction solutions.

<u>Reaction solution A1</u>	
Magnesium acetate hexahydrate (magnesium acetate 14.8% by weight)	25% by weight
Diethylene glycol	10% by weight
Pure water	Balance
<u>Reaction solution A2</u>	
Calcium chloride	10% by weight
Diethylene glycol	10% by weight
Pure water	Balance

Reaction solution A3

The following dyes were added to the following liquid medium to prepare reaction solutions serving also as cyan, magenta, and yellow color ink compositions.

<u>Dye</u>		
Cyan ink	3% by weight	60
C.I. Direct Blue 86		
Magenta ink	3% by weight	
C.I. Direct Red 9		
Yellow ink	3% by weight	
C.I. Acid Yellow 23		65
Liquid medium		
Calcium chloride	10% by weight	
Glycerin	10% by weight	
Pure water	Balance	

The above ink compositions and reaction solutions were combined as specified in Table 1, and the combinations were evaluated by tests described below.

TABLE 1

	Black ink	Color ink set	Reaction solution
Example			
A-1	A1	—	A1
A-2	A2	—	A2
A-3	A3	—	A2
A-4	A4	—	A2
A-5	A5	—	A1
A-6	A1	A1	A2
A-7	A1	A2	A2
A-8	A1	—	A3
A-9	A1	—	—
Comparative Example			
A1	A5	—	—
A2	A6	—	A2
A3	A6	—	—

Evaluation A1: Print quality (feathering)

An ink jet printer MJ-700V2C (manufactured by Seiko Epson Corporation) was used to perform printing on the following various papers. In the printing, the reaction solution was first printed (100% duty), and the black ink was then used to print a letter. After drying, the prints were inspected for feathering in the letter.

- (1) Xerox P Paper (Xerox Corp.)
- (2) Ricopy 6200 Paper (Ricoh Co. Ltd.)
- (3) Xerox 4024 Paper (Xerox Corp.)
- (4) Neenah Bond Paper (Kimberly-Clark)
- (5) Xerox R Paper (recycled paper, Xerox Corp.)
- (6) Yamayuri (recycled paper, Honshu Paper Co., Ltd.)

The results were as tabulated in Table 2. Regarding the results given in the table, the evaluation criteria are as follows.

- o: Sharp print without any feathering
- Δ: Feathering observed
- X: Remarkable feathering observed rendering the outline of the letter blurry

Evaluation A2: Unevenness of printing

An ink jet printer MJ-700V2C was used to perform printing (100% duty) on the following various papers. The printing method was the same as described above in connection with the evaluation of the print quality (feathering).

- (1) Ricopy 6200 Paper (Ricoh Co. Ltd.)
- (2) Canon dry Paper (Canon Inc.)

For the resultant print images, the reflection OD was measured with Macbeth PCMI (manufactured by Macbeth). This measurement was performed for randomly selected five points in the print area, and the average of the measured values was determined. This procedure was repeated five times, and the maximum value and the minimum value in the five average values were determined. When the difference between the maximum value and the minimum value is less than 0.5, there is no problem for practical use with the difference being preferably less than 0.4. The results were as tabulated in Table 2. In the results given in the; table, the evaluation criteria were as follows.

- o: OD difference of less than 0.3
- Δ: OD difference of 0.3 to less than 0.4
- X: OD difference of not less than 0.4

Evaluation A3: Rubbing property

An ink jet printer MJ-700V2C was used to perform printing on Xerox P paper (manufactured by Xerox Corp.), and the resultant prints were air-dried for 24 hr. The prints

were rubbed with a finger under an environment of 25° C. and 50% RH and then observed by visible inspection for the presence of a stain on the print. The results were as tabulated in Table 2. In the table, the evaluation criteria were as follows.

- o: No stain observed in the print
- Δ: Slight stain observed in the print with the letter being still legible
- X: Stain observed in the print rendering the letter illegible

Evaluation A4: Color bleeding

An ink jet printer MJ-700V2C was used in this evaluation test. The reaction solution was deposited (100% duty) on the following recording media, and color inks (cyan, magenta, and yellow) (100% duty) and the black ink (a letter) were simultaneously printed to examine the prints for the presence of uneven color-to-color mixing in the letter boundaries. In this case, in Example 8, the reaction solution (100% duty) and the black ink (a letter) were simultaneously printed.

- (1) Xerox P Paper (Xerox Corp.)
- (2) Ricopy 6200 Paper (Ricoh Co. Ltd.)
- (3) Xerox 4024 Paper (Xerox Corp.)
- (4) Neenah Bond Paper (Kimberly-Clark)
- (5) Xerox R Paper (recycled paper, Xerox Corp.)
- (6) Yamayuri (recycled paper, Honshu Paper Co.)

The results were as tabulated in Table 2. In the table, the evaluation criteria were as follows.

- o: No color-to-color mixing observed with clear letter boundaries
- Δ: Feather-like color-to-color mixing observed
- X: Significant color-to-color mixing observed rendering the outline of the letter blurry.

Evaluation A5: Fixability onto specialty media

An ink jet printer MJ-700V2C was used to print an ink on a specialty gloss paper for MJ-700V2C (manufactured by Seiko Epson Corporation), and the resultant prints were air-dried for 24 hr. The prints were rubbed with a finger under an environment of 25° C. and 50% RH and then visually inspected for the presence of a stain on the print and the separation of the colorant. The results were as tabulated in Table 2. In the table, the evaluation criteria were as follows.

- o: Neither stain nor separated colorant observed in the print
- Δ: Slight stain observed in the print with separated colorant not observed in the print
- X: Both stain and separated colorant observed in the print

TABLE 2

Example	Evaluation				
	A1	A2	A3	A4	A5
A1	○	○	○	—	—
A2	Δ	○	○	—	—
A3	○	○	○	—	—
A4	Δ	○	○	—	—
A5	Δ	○	○	—	—
A6	○	○	○	Δ	Δ
A7	○	○	○	○	○
A8	○	○	○	Δ	Δ
A9	—	—	—	—	—

TABLE 2-continued

Comparative Example	Evaluation					
	A1	A2	A3	A4	A5	
A1	X	Δ	Δ	—	—	5
A2	Δ	X	X	—	—	10
A3	—	—	—	—	X	

The following ink compositions were prepared.

Black ink B1			
Carbon black MA7 (manufactured by Mitsubishi Kasei Corp.)	5% by weight		20
Styrene/acrylic acid copolymer (dispersant)	1% by weight		
Almatex Z116 (epoxy-containing acrylic resin emulsion, resin content 50%, manufactured by Mitsui Toatsu Chemicals, Inc.)	3% by weight		
Snowtex S (colloidal silica, SiO ₂ content 30%, manufactured by Nissan Chemical Industry Ltd.)	2% by weight		25
Sucrose	0.7% by weight		
Maltitol	6.3% by weight		
Glycerin	10% by weight		
2-Pyrrolidone	2% by weight		
Triethanolamine (pH adjustor)	1.0% by weight		
KOH (pH adjustor)	0.1% by weight		30
Pure water	Balance		
Black ink B2			
Carbon black Raven 1080 (manufactured by Columbian Carbon Co., Ltd.)	5% by weight		40
Styrene/acrylic acid copolymer (dispersant)	1% by weight		
Almatex Z116 (epoxy-containing acrylic resin emulsion, resin content 50%, manufactured by Mitsui Toatsu Chemicals, Inc.)	3% by weight		
Epilight 400E (water-soluble epoxy compound, polyethylene glycol #400 glycidyl ether, manufactured by Kyoeisha Chemical Co., Ltd.)	2% by weight		45
Snowtex C (colloidal silica, SiO ₂ content 20%, manufactured by Nissan Chemical Industry Ltd.)	1% by weight		
Sucrose	0.7% by weight		
Maltitol	6.3% by weight		
Glycerin	10% by weight		
2-Pyrrolidone	2% by weight		
Ethanol	4% by weight		
Pure water	Balance		
Black ink B3			
Carbon black Raven 1080	5% by weight		60
Styrene/acrylic acid copolymer (dispersant)	1% by weight		
Microgel E-5002 (styrene/acrylic resin emulsion, resin content 29.2%, MFT about 80° C., manufactured by Nippon Paint Co., Ltd.)	3.5% by weight		

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Almatex Z116 (epoxy-containing acrylic resin emulsion, resin content 50%, manufactured by Mitsui Toatsu Chemicals, Inc.)	5% by weight		
Snowtex S	1% by weight		
Sucrose	0.7% by weight		
Maltitol	6.3% by weight		
Glycerin	10% by weight		
2-Pyrrolidone	2% by weight		
Triethanolamine (pH adjustor)	1.0% by weight		
KOH (pH adjustor)	0.1% by weight		
Pure water	Balance		
Black ink B4			
Carbon black Raven 1080 (manufactured by Columbian Carbon Co., Ltd.)	5% by weight		
Styrene/acrylic acid copolymer (dispersant)	1% by weight		
Microgel E-5002 (styrene/acrylic resin emulsion, resin content 29.2%, MFT about 80° C., manufactured by Nippon Paint Co., Ltd.)	3.5% by weight		
Epilight 400E (water-soluble epoxy compound, polyethylene glycol #400 glycidyl ether, manufactured by Kyoeisha Chemical Co., Ltd.)	2% by weight		25
Snowtex C (colloidal silica, SiO ₂ content 20%, manufactured by Nissan Chemical Industry Ltd.)	1% by weight		
Sucrose	0.7% by weight		
Maltitol	6.3% by weight		
Glycerin	10% by weight		
2-Pyrrolidone	2% by weight		
Ethanol	4% by weight		
Pure water	Balance		35
Black ink B5			
Carbon black Raven 1080 (manufactured by Columbian Carbon Co., Ltd.)	5% by weight		40
Styrene/acrylic acid copolymer (dispersant)	1% by weight		
Sucrose	0.7% by weight		
Maltitol	6.3% by weight		
Glycerin	10% by weight		
2-Pyrrolidone	2% by weight		
Ethanol	4% by weight		
Pure water	Balance		45
Black ink B6			
Carbon black Raven 1080 (manufactured by Columbian Carbon Co., Ltd.)	5% by weight		50
Styrene/acrylic acid copolymer (dispersant)	1% by weight		
Microgel E-5002 (styrene/acrylic resin emulsion, resin content 29.2%, MFT about 80° C., manufactured by Nippon Paint Co., Ltd.)	3.5% by weight		
Sucrose	0.7% by weight		
Maltitol	6.3% by weight		
Glycerin	10% by weight		
2-Pyrrolidone	2% by weight		
Ethanol	4% by weight		
Pure water	Balance		60

The above black inks were prepared as follows. Carbon black and the dispersant were mixed together and dispersed by means of a sand mill (manufactured by Yasukawa Seisakusho) with glass beads (diameter: 1.7 mm, amount: 1.5 times, by weight, the amount of the mixture) for 2 hr..

Thereafter, the glass beads were removed, and the remaining additives were added, and the mixture was stirred at room temperature for 20 min and then filtered through a 5- μ m membrane filter to prepare an ink for ink jet recording.

Color ink set B1

Color ink set B1	
<u>Cyan ink</u>	
Pigment KETBLUEEX-1 (manufactured by Dainippon Ink and Chemicals, Inc.)	2% by weight
Styrene/acrylic acid copolymer (dispersant)	1% by weight
Almatex Z116 (epoxy-containing acrylic resin emulsion, resin content 50%, manufactured by Mitsui Toatsu Chemicals, Inc.)	3% by weight
Snowtex S (colloidal silica, SiO ₂ content 30%, manufactured by Nissan Chemical Industry Ltd.)	2% by weight
Sucrose	0.7% by weight
Maltitol	6.3% by weight
Glycerin	10% by weight
2-Pyrrolidone	2% by weight
Ethanol	4% by weight
Pure water	Balance
<u>Magenta ink</u>	
Pigment KETRED309 (manufactured by Dainippon Ink and Chemicals, Inc.)	2% by weight
Styrene/acrylic acid copolymer (dispersant)	1% by weight
Almatex Z116 (epoxy-containing acrylic resin emulsion, resin content 50%, manufactured by Mitsui Toatsu Chemicals, Inc.)	3% by weight
Snowtex S (colloidal silica, SiO ₂ content 30%, manufactured by Nissan Chemical Industry Ltd.)	2% by weight
Sucrose	0.7% by weight
Maltitol	6.3% by weight
Glycerin	10% by weight
2-Pyrrolidone	2% by weight
Ethanol	4% by weight
Pure water	Balance
<u>Yellow ink</u>	
Pigment KETYELLOW403 (manufactured by Dainippon Ink and Chemicals, Inc.)	2% by weight
Almatex Z116 (epoxy-containing acrylic resin emulsion, (resin content 50%), manufactured by Mitsui Toatsu Chemicals, Inc.)	3% by weight
Snowtex S (colloidal silica, (SiO ₂ content 30%), manufactured by Nissan Chemical Industry Ltd.)	2% by weight
Sucrose	0.7% by weight
Maltitol	6.3% by weight
Glycerin	10% by weight
2-Pyrrolidone	2% by weight
Ethanol	4% by weight
Pure water	Balance
<u>Color ink set B2</u>	
<u>Cyan ink</u>	
Pigment KETBLUEEX-1 (manufactured by Dainippon Ink	2% by weight

-continued

5	and Chemicals, Inc.) Styrene/acrylic acid copolymer (dispersant)	1% by weight
	Sucrose	0.7% by weight
	Maltitol	6.3% by weight
	Glycerin	10% by weight
	2-Pyrrolidone	2% by weight
10	Ethanol	4% by weight
	Pure water	Balance
	<u>Magenta ink</u>	
	Pigment KETRED309 (manufactured by Dainippon Ink and Chemicals, Inc.)	2% by weight
	Styrene/acrylic acid copolymer (dispersant)	1% by weight
15	Sucrose	0.7% by weight
	Maltitol	6.3% by weight
	Glycerin	10% by weight
	2-Pyrrolidone	2% by weight
	Ethanol	4% by weight
20	Pure water	Balance
	<u>Yellow ink</u>	
	Pigment KETYELLOW403 (manufactured by Dainippon Ink and Chemicals, Inc.)	2% by weight
	Sucrose	0.7% by weight
	Maltitol	6.3% by weight
25	Glycerin	10% by weight
	2-Pyrrolidone	2% by weight
	Ethanol	4% by weight
	Pure water	Balance
	<u>Yellow ink</u>	
30	Pigment KETYELLOW403 (manufactured by Dainippon Ink and Chemicals, Inc.)	2% by weight
	Sucrose	0.7% by weight
	Maltitol	6.3% by weight
	Glycerin	10% by weight
	2-Pyrrolidone	2% by weight
35	Ethanol	4% by weight
	Pure water	Balance
	<u>Yellow ink</u>	
	Pigment KETYELLOW403 (manufactured by Dainippon Ink and Chemicals, Inc.)	2% by weight
	Almatex Z116 (epoxy-containing acrylic resin emulsion, (resin content 50%), manufactured by Mitsui Toatsu Chemicals, Inc.)	3% by weight
40	Snowtex S (colloidal silica, (SiO ₂ content 30%), manufactured by Nissan Chemical Industry Ltd.)	2% by weight
	Sucrose	0.7% by weight
	Maltitol	6.3% by weight
	Glycerin	10% by weight
	2-Pyrrolidone	2% by weight
45	Ethanol	4% by weight
	Pure water	Balance
	<u>Yellow ink</u>	
	Pigment KETYELLOW403 (manufactured by Dainippon Ink and Chemicals, Inc.)	2% by weight
	Almatex Z116 (epoxy-containing acrylic resin emulsion, (resin content 50%), manufactured by Mitsui Toatsu Chemicals, Inc.)	3% by weight
50	Snowtex S (colloidal silica, (SiO ₂ content 30%), manufactured by Nissan Chemical Industry Ltd.)	2% by weight
	Sucrose	0.7% by weight
	Maltitol	6.3% by weight
	Glycerin	10% by weight
	2-Pyrrolidone	2% by weight
55	Ethanol	4% by weight
	Pure water	Balance
	<u>Yellow ink</u>	
	Pigment KETYELLOW403 (manufactured by Dainippon Ink and Chemicals, Inc.)	2% by weight
	Almatex Z116 (epoxy-containing acrylic resin emulsion, (resin content 50%), manufactured by Mitsui Toatsu Chemicals, Inc.)	3% by weight
60	Snowtex S (colloidal silica, (SiO ₂ content 30%), manufactured by Nissan Chemical Industry Ltd.)	2% by weight
	Sucrose	0.7% by weight
	Maltitol	6.3% by weight
	Glycerin	10% by weight
	2-Pyrrolidone	2% by weight
65	Ethanol	4% by weight
	Pure water	Balance

The above color ink compositions were prepared as follows. The pigment and the dispersant were mixed together and dispersed by means of a sand mill (manufactured by Yasukawa Seisakusho) with glass beads (diameter: 1.7 mm, amount: 1.5 times, by weight, the amount of the mixture) for 2 hr. Thereafter, the glass beads were removed, and the remaining additives were added, and the mixture was stirred at room temperature for 20 min and then filtered through a 5- μ m membrane filter to prepare an ink composition.

Reaction solution B1

45	Magnesium nitrate hexahydrate	25% by weight
	Triethylene glycol monobutyl ether	10% by weight
	Glycerin	20% by weight
	Pure water	Balance

Reaction solution B2

50	Magnesium nitrate hexahydrate	25% by weight
	Water-soluble polyamine (Almatex H700, manufactured by Mitsui Toatsu Chemicals, Inc.)	3% by weight
	Triethylene glycol monobutyl ether	10% by weight
	Glycerin	20% by weight
55	Pure water	Balance

The above reaction solutions were prepared by mixing the ingredients together, stirring the mixture at room temperature for one hr, and subjecting the stirred mixture to suction filtration through a 5 μ m-membrane filter at room temperature.

Print evaluation test

Predetermined printing was carried out using combinations of the above ink compositions with the above reaction solutions. The printed images thus obtained were evaluated as follows.

Printing method

An ink jet printer MJ-700V2C (manufactured by Seiko Epson Corporation) was used to perform printing on the following various papers. In the printing, the reaction solution was first printed (100% duty), and the black ink was used to print a letter. In this case, for both the reaction solution and the ink, the amount of the ink ejected was 0.07 $\mu\text{g}/\text{dot}$ with the density being 360 dpi. Papers for printing test:

- (1) Xerox P Paper (Xerox Corp.)
- (2) Ricopy 6200 Paper (Ricoh Co. Ltd.)
- (3) Xerox 4024 Paper (Xerox Corp.)
- (4) Neenah Bond Paper (Kimberly-Clark)
- (5) Xerox R Paper (recycled paper, Xerox Corp.)
- (6) Yamayuri (recycled paper, Honshu Paper Co., Ltd.)

Evaluation B1: Rubbing resistance test (line marking resistance)

The resultant prints were air-dried and then rubbed with a water-base yellow fluorescent marker pen (ZEBRA PEN 2, manufactured by ZEBRA) at a marking force of $4.9 \times 10^5 \text{ N/m}^2$, and the degree of stain in the yellow area was visually inspected. The results were evaluated based on the following criteria.

- ⊙: No stain created by marking twice immediately after printing
- : No stain created by marking twice 24 hr after printing
- Δ: No stain created by marking once with some paper being stained by marking twice or 24 hr after printing
- X: Some paper stained by marking once 24 hr after printing

Evaluation B2: Print quality (feathering)

Letters after drying the resultant prints were inspected for feathering, and the results were evaluated as follows.

- ⊙: Sharp without any feathering for all the papers
- : Feathering observed for some papers (recycled paper)
- Δ: Feathering observed for all the papers
- X: Remarkable feathering observed rendering the outline of the letter blurry

Evaluation B3: OD value

The reflection optical density (OD) of prints provided by the above method was measured with Macbeth PCMII (manufactured by Macbeth).

The reaction solutions and the ink compositions used in the evaluations B1 to B3, and the results of evaluation were as tabulated in Table 3.

TABLE 3

	Reaction	Black	Evaluation		
	solution	ink	B1	B2	B3
<u>Example</u>					
B1	B1	B1	○	⊙	1.65
B2	B1	B2	○	⊙	1.62
B3	B1	B3	○	⊙	1.60
B4	B1	B4	○	⊙	1.59
B5	B2	B1	⊙	⊙	1.68
B6	B2	B2	⊙	⊙	1.65
B7	B2	B3	⊙	⊙	1.63
B8	B2	B4	⊙	⊙	1.62
<u>Comparitive Example</u>					
B1	B1	B5	X	X	1.32
B2	B1	B6	Δ	○	1.42

Evaluation B4: Color bleed

An ink jet printer MJ-700V2C was used in this evaluation test. The reaction solution was deposited (100% duty) on the above various papers as a recording paper, and color inks (cyan, magenta, and yellow) (100% duty) were simultaneously printed. The prints were visually inspected for the presence of uneven color-to-color mixing in the boundaries between the colors. The results were evaluated based on the following criteria:

- : No color-to-color mixing observed.
 - Δ: Feather-like color-to-color mixing observed.
 - X: Significant color-to-color mixing observed.
- The results were as tabulated in Table 4.

TABLE 4

	Reaction solution	Color ink set	Evaluation B4
Example			
B9	B1	B1	○
B10	B2	B1	○
Comparative Example			
B3	B1	B2	X

Evaluation B5: Fixation of ink on specialty medium (part 1)

An ink jet printer MJ-700V2C (manufactured by Seiko Epson Corporation) was used to perform printing on a specialty gloss film for the ink jet printer MJ-700V2C (manufactured by Seiko Epson Corporation), and the resultant prints were air-dried for 24 hr. The prints were examined in the same manner as described in Evaluation B1. The results were evaluated based on the following criteria:

- : No stain created in the print by rubbing once
- Δ: Slight stain created in the print by rubbing once
- X: Stain created in the print by rubbing once

Evaluation B6: Fixation of ink on specialty medium (part 2)

A pressure-sensitive adhesive tape (cellophane tape: Sekisui Tape, manufactured by Sekisui Chemical Co., Ltd.) was applied to the printed area in the prints, rubbed twice or thrice with a finger, and then peeled off. Thereafter, the printed area from which the pressure-sensitive adhesive tape has been peeled off was visually inspected, and the results were evaluated based on the following criteria:

- : Ink (colorant) not separated from the surface of the specialty gloss film
 - Δ: Ink present in both the surface of the specialty gloss film and the surface of a pressure-sensitive adhesive in the pressure-sensitive adhesive tape
 - X: Ink (colorant) completely separated from the surface of the specialty gloss film
- The results were as tabulated in Table 5.

TABLE 5

	Black ink	Evaluation B5	Evaluation B6
Example			
B11	B1	○	○
B12	B2	○	○
B13	B3	○	○
B14	B4	○	○